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Review

Towards “user-friendly” heavier primary pnictanes: Recent developments in the chemistry of primary phosphines, arsines and stibines☆

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Contents

Abstract

Primary pnictanes (phosphines, arsines and stibines) are valuable starting materials in many reactions. In this article, an account is given of recent developments in the chemistry of “user-friendly” primary pnictanes, with emphasis on the use of the bulky substituents for their

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Abbreviations: Ad, 1-adamantyl; Andbb, acenaphthenedibenzobarellene; Anth, anthracenyl; Arf, 2,6-bis(trifluoromethyl)phenyl; Artipp, 2,6-Tipp$_2$C$_6$H$_3$; Arx, *p*-^{t}Bu-phenyl; Cp, cyclopentadienyl (C$_5$H$_5$); Cp^o, ethyltetramethylcyclopentadienyl (C$_5$EtMe$_4$); Cp*, pentamethylcyclopentadienyl (C$_5$Me$_5$); Cp′, methylcyclopentadienyl (C5H4Me); Cy, cyclohexyl; Dbb, dibenzobarellene; Dimet, 2,6-dimesityl-4-methylphenyl; Dipp, 2,6-^{i}Pr$_2$C$_6$H$_3$; Dnp, 2,6-di-1-naphthylphenyl; DOC, 2,6-dimethyl-4-octoxyphenyl; Dpdbb, diphenyldibenzobarellene; Es, 2,4,6-triethylC$_6$H$_2$; Fc, ferrocenyl (C$_5$H$_4$FeC$_5$H$_5$); Is, 2,4,6-triisopropylphenyl; J_{PH}, phosphorus-proton coupling constant; Mes, 2,4,6-Me$_3$C$_6$H$_2$; Mes*, 2,4,6-^{t}Bu$_3$C$_6$H$_2$; MesEt, 2,4,6-Et$_3$C$_6$H$_2$; NM, neomenthyl; Pa, phenylacetyl; Pi, pinen-fused; Pip, piperidine; QM, quantum mechanical; Ph, phenyl; Phes, 2,4,6-triphenylphenyl; *p*-Tol, *para*-tolyl; Ru^4, Ruthenium porphyrine derivative (see Section 2.4.5); Tetraphos, [P(CH$_2$CH$_2$PPh$_2$)$_3$]; Tipp (also Is or Trip), 2,4,6-^{i}Pr$_3$C$_6$H$_2$; Triphos, MeC(CH$_2$PPh$_2$)$_3$; Tript, triptycene (tribenzobarellene); Trt, trityl (C(Ph)$_3$)

☆ In memoriam: Axel Christian Klixbull Jørgensen (1931–2001), great humanist, fascinating scientist and humble teacher.

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stabilization. Available structural parameters, as well as several physico-chemical properties such as melting points and sensitivity towards air and moisture, are collected and discussed. Also included is a brief survey of ^{31}P NMR data for primary phosphines and their organotransition metal complexes.

Keywords: User-friendly; Primary phosphines; Organotransition metal complexes

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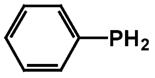
1. Introduction

Because of their importance as starting materials or active intermediates in many reactions, there is a growing interest in the employment of the "user-friendly" primary hydrogen derivatives of the heavier Group 15 elements such as primary phosphines, arsines and stibines [1,2]. The purpose of this short review is to survey recent data for compounds of this type that are stabilized by large substituents that confer increased air and/or thermal stability. The following sections are essentially dedicated to a broad spectrum of compounds with such properties. Emphasis is placed on the role of the bulky substituents in their stabilization. In addition, physical and certain spectroscopic properties are presented, together with brief structural analysis of the available X-ray structures. Although the review focuses mainly on the air-stable species, interesting primary phosphines with less oxidative inertness are also mentioned. Synthetic procedures leading to the primary phosphines (or their arsenic and antimony homologues) are omitted here, and the reader can find general information on this topic in dedicated reviews or monographs [1,3]. Two short sections are also concerned with a brief survey of the ^{31}P NMR spectral data and the dynamic phenomena related to the hindered rotation of the PH_2 group in solution.

Primary pnictanes of the form $R–EH_2$ (E = P, As, Sb and Bi), particularly those containing small alkyl groups, are usually highly air-sensitive, and often pyrophoric. They are also highly toxic, and exhibit a characteristic, intense unpleasant odor, making their use in synthesis rather difficult and often hazardous. As recently noted by several authors [2,4], compounds of this type with more "user-friendly" characteristics are attracting unceased attention. The "ideal" compound would be an odorless, easily stored solid or liquid, with good thermal stability, and very low air- and water-sensitivity. This would allow manipulations during synthetic steps or purifications to be carried out in aerobic conditions using standard chromatographic techniques and no use of protecting groups on pnictogen should be necessary to maintain the integrity of the EH_2 group. In the last few years, the number of reported air-stable primary pnictanes has grown rapidly through the use of bulky substituents for the kinetic stabilization of these species. Both aryl and alkyl sterically demanding substituents have been probed, or even specifically designed to stabilize free primary pnictanes. This approach has also been used for the isolation of compounds with double bonds involving second row, main group elements [5] or alkyne analogues [6,7] of Ge and Sn. Primary phosphines have also been stabilized by their complexation with boranes and a new class of organotransition metal complexes of these usually unstable species has also been synthesized.

As recently pointed out by Power and co-workers [8], the bond enthalpies for the E–H bonds in the Group 15 pnictanes remain surprisingly large for the heavier group members (e.g., Sb–H ca. 60 kcal mol^{-1}), even if they display increasingly positive values for $\Delta G_{\mathrm{f}}^{\circ}$, as the group is descended. This trend indicates that they could be kinetically stabilized by the use of sterically crowded substituents. This observation is clearly confirmed by a quick analysis of the physico-chemical properties of a series of aryl arsines and phosphines where the EH_2 (E = P, As) group is connected to a phenyl ring with ortho-flanking substituents of increasing size. Phenylstibane, $PhSbH_2$, decomposes at room temperature [9], whereas ^{t}BuCH$_2$SbH$_2$ [10] and $Me_3SiCH_2SbH_2$ [11] are colorless liquids, which are stable for long periods under a hydrogen atmosphere at room temperature. The analogous observation is even more striking in the case of primary phosphines:



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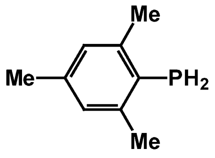

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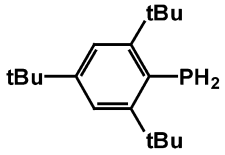

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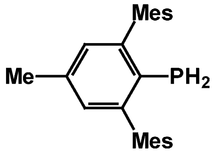

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While **1** is a pyrophoric, extremely air-sensitive liquid [12] with a foul odor, **2** shows already a moderate air-stability [13]. Enhanced steric protection resulting from introduction of the ^{t}Bu group on the central ring is observed in **3** [14] (sometimes called "supermesitylphosphine" or Mes*PH$_2$), which in the solid state can be considered quite air-stable although it will oxidize slowly over several months. Phosphine **4**, which bears two bulky mesityl groups at the *ortho* position to the phosphorus atom [15], is a white solid, completely inert towards oxidation, with an elevated melting point close to 213 °C.

The differences in the reactivity of the primary versus tertiary phosphines are due to the presence of the two "acidic" P–H bonds [16]; these reactive sites are not available in tertiary phosphines R_3P. Primary phosphines are expected to be weaker donors than tertiary phosphines due to an increased s character of the P lone pair orbital. The reactivity of the phosphine ligands is related to the electron-donating and electron-accepting properties of the phosphorus atom as well as of the steric effects of the substituents, and different models have been proposed to quantify these electronic and steric effects. These are based on some key phosphine properties such as cone and bite angles, and basicity [17–21].

Before reviewing the physico-chemical characteristics and available structural data of the title compounds, it is worth briefly discussing their simple hydride precursors: PH_3, AsH_3, SbH_3 and BiH_3. The first three are known to be extremely toxic, and volatile gaseous substances, spontanously flammable in an oxygen atmosphere. The existence of bismuth hydride or bismuthine (BiH_3), which is usually described as an unstable Group 15 hydride with a low boiling point (−16.8 °C), was controversial for many years. Only very recently were the early experiments of Amberger [22] repeated, and with the help of modern spectroscopic methods supported by ab initio calculations, was this unstable entity unambiguously characterized [23,24].

The most relevant physico-chemical characteristics of the EH_3 derivatives of pnictogens are presented in Table 1. As can be seen from the corresponding data, whereas structural characteristics are similar for all of the four gases, the E–H bond length decreases from heavier to lighter elements, varying from 1.78 Å in BiH_3 to 1.42 Å in PH_3. The pyramidality of the EH_3 is more pronounced when descending the group (93.5° for PH_3 versus 90.5° for BiH_3), a lone pair containing two electrons being centered on the heavy atom. These geometric characteristics are only slightly affected in free organic primary pnictane hydrides. For example, in the crystalline $DbbPH_2$ the P–H bond is 1.36(3) Å and the HPH angle ca. 93(2)°.

2. Primary phosphines

2.1. Free primary mono-phosphines

Despite their rather unfriendly characteristics, primary phosphines are recognized as having a broad spectrum of applications. They can act as starting materials for enantiomerically pure phosphetanes [25], phosphiranes [26] or phospholanes [27], as well as precursors for niobium phosphide (NbP) films [28] or peptide chain homologues [1]. They also have potential catalytic and biomedical applications, for example, as antitumor agents [29]. Until a few years ago, primary phosphines were generally considered to be air- and moisture-sensitive liquid or gaseous compounds. Although they are generally unreactive towards water, their moisture-sensivity is often the result of a reaction with dissolved oxygen. The current interest in more robust chemicals of this class of compounds is of recent origin; with respect to the variety of applications, these synthetic intermediates can offer both in biochemistry and catalysis. The first attempt to stabilize primary phosphines with sterically encumbring substituents was undertaken in the late 1960s. In 1969, Stetter and Last synthesized adamantylphosphine [30] ($AdPH_2$), which was obtained as an oxygen sensitive liquid with a low boiling point and a characteristic refellent odor. The last few years have seen rapid growth in the chemistry of these species, with the appearence of more stable, solid primary phosphines. The majority of the reported crystal structures having an $R{-}PH_2$ moiety have been determined as complexes where the phosphorus atom is coordinated to a metal atom. The crystal structures of free mono-primary phosphines are less abundant and have only been obtained in a limited number of cases: where the phosphorus atom is bound to a cumbersome protective aryl group, to a bulky alkyl group such as a triptycyl or dibenzobarellene moiety, or to a ferrocenyl

Table 1
Selected physico-chemical data for the EH_3 derivatives of pnictogens

E	P	As	Sb	Bi[a]
EH bond length (Å)	1.4200	1.511	Sb–H, 1.7073 ± 0.0025	1.7759[b]
HEH bond angle (°)	93.345	91.6	HSbH, 91.30 ± 0.33	90.48[b]
ΔG_f°	3.20	16.46	35.31	–
ΔH_f°	1.29	15.39	34.66	–
EH bond enthalpy	70.9	65.5	60.0	67.6
Properties of EH_3				
Color	Colorless	Colorless	Colorless	Colorless
Appearance	Gas	Gas	Gas	Gas
Melting point (°C)	−133	−116	−88	
Boiling point (°C)	−88	−62.5	−17	17
Density (kg m^{-3})	1.5 (gas)	3.42	5.48 (gas)	9.3 (gas)

ΔH_f°: standard molar enthalpy (heat) of formation at 298.15 K in kJ/mol; ΔG_f°: standard molar Gibbs energy of formation at 298.15 K in kJ/mol; EH bond enthalpy in kcal/mol.

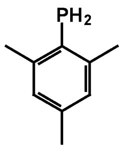
[a] The data are from Ref. [129].

[b] The data are from Ref. [24].

group. Other free, stable primary phosphines include various bisphosphines attached to aryl groups, fluoroalkylphosphines or *N*-quaternised aminoalkylphosphines.

2.1.1. *Aryl phosphines*

Mesitylphosphine **2**, one of the first, moderately air-stable aryl primary monophosphines, was synthesized by Becker et al. [13] by the reduction of $MesPCl_2$ with $LiAlH_4$. Ten years later, **2** became the first primary phosphine characterized by X-ray crystallography in Power and co-workers [31]. Earlier attempts to characterize primary phosphines focused on gas-phase techniques involving electron diffraction or microwave spectroscopy [23,24,32–34]. $MesPH_2$ crystallizes in the orthorombic system, and consists of parallel layers of molecules, spaced by about 3.5 Å, in which no significant H-bonding between phosphorus and hydrogen atoms occurs, although the hydrogen atoms bonded to P could not be located with certainty. The P–C bond was found to be 1.807(5) Å, in accordance with previously obtained values. Modification of the size or the shape of the protecting aryl group, to assure better kinetic stabilization of the PH_2 group, resulted in a series of analogous bulky aryl phosphines. The group of Yoshifuji and co-workers reported the synthesis of RPH_2 derivatives where R is sterically bulky (R = 2,6-dimesityl-4-methylphenyl, Dimet) [15], as shown in compound **4**. This compound is completely stable towards oxidation and has an elevated melting point close to 213 °C. It can be handled and purified on silica columns without any particular precaution at open air atmosphere, and is easily recrystallized from common organic solvents. This phosphine has been used extensively as an intermediate for many reactions, unfortunately its crystal structure has not yet been reported. In the same class, 2,4,6-tri-*t*-butylphenylphosphine **3** has been widely used in a number of synthetic schemes, leading, for example, to crystalline monophosphaallenes [35] or phosphaalkenes [36,37]. Power and co-workers reported the bulky $ArtippPH_2$ **14**, which is completely stable in air and characterized by a mp of 215–218 °C [8]. Compound **14** possess a plane of symmetry perpendicular to the central aryl ring plane, which incorporates the *ipso* and *para* carbon and the pnictane atom.



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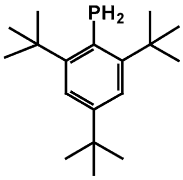

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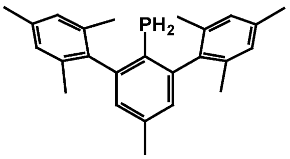

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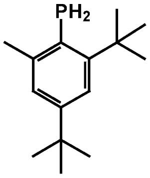

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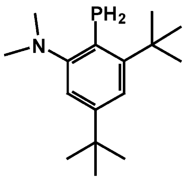

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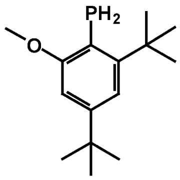

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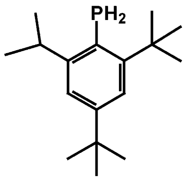

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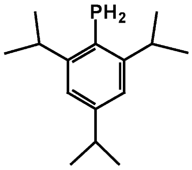

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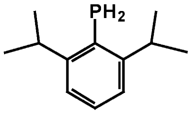

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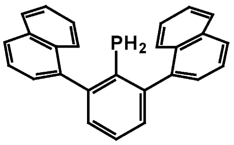

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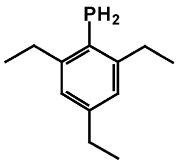

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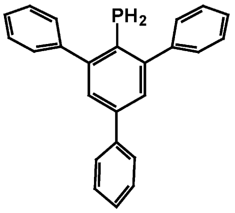

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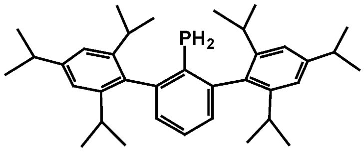

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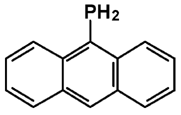
Yoshifuji and co-workers have also been successful in preparing several derivatives of 2,4-^{t}Bu-phenyl phosphines with substituents of different steric hindrance at the 6 position [14,38–42] (**3**,**5**–**8**). In the ^{31}P NMR spectrum, **5** and **8** are shifted upfield by 12–13 ppm compared to **3**. Most likely, the electron-donating effect of the phosphorus-binding hydrogen atoms in **3** is not as effective as that of **8**.

Other aryl phosphines were also reported with isopropyl or ethyl moieties as flanking substituents, but their air- and moisture-sensitivity is less interesting since the presence of these latter groups on the central phenyl ring provides only moderate steric protection. Known derivatives of this type [43,44] include 2,4,6-tri-isopropylphenylphosphine ($IsPH_2$) **9**, 2,4,6-triethylphenylphosphine ($EsPH_2$) **12** and 2,6-dimethyl-4-octoxyphenylphosphine ($DOCPH_2$). All are colorless liquids (bp 77, 77 and 120 °C at 3 mbar, respectively). 2,4,6-Triphenylphenylphosphine (PhesPH$_2$) **13** was obtained as colorless crystals (mp 64 °C) and can be easily stored in air for several weeks.

A variation of **9**, 2,6-di-isopropylphenylphosphine [45], DippPH$_2$ **10** which differs from **9** only by the absence of the isopropyl group at the *para* position, has been prepared as a clear oil (bp 73–85 °C, 0.5 mbar) by reaction of Mg(2,6-di-isopropylbenzene)bromide with PCl$_3$ and subsequent reduction with LiAlH$_4$. This colorless liquid is reported to have very little odor but its oxidative stability is low and it must be stored under nitrogen to avoid oxidation. A ^{31}P NMR signal corresponding to the phosphine oxide, DippP(O)H$_2$, formed by aerobic oxidation of the phosphine, was detected after repeated handling of a container of **10**. An interesting molecular framework was used to protect the PH$_2$ fragment in 2,6-di-1-naphthylphenyl phosphine **11** (DnpPH$_2$), which contains two flanking, large naphthalene units [46]. Although the crystal structure of this compound has not been reported, its dimeric lithium derivative bis[μ-bis(2,6-di-1-naphthylphenyl)-phosphanido]bis[(tetrahydrofuran)lithium(I)] [46] showed that the planes containing the two flanking naphthalene units make angles of 75° and 80° with respect to the plane containing central phenyl ring, assuring steric protection of the PH bond in a way similar to that observed in **14** [8].

Air-sensitivity is dramatically affected in the absence of the bulky flanking substituents at *ortho* positions. For example, 9-anthracenylphosphine [47] **15** reported by Schmutzler and co-workers, was obtained as a yellowish solid with a melting point of 88 °C and moderate oxidative stability. In solution, **15** undergoes a rapid oxidation to anthraphosphonic acid AnthPO(OH)$_2$, which can be easily monitored by ^{31}P NMR. Attemps to obtain single crystals of this compound in our group failed, probably as a result of its slow oxydation in solution during the crystallization process.



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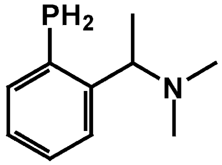
Other primary aryl monophosphines should also be mentioned. These include enantiomeric primary phosphines with a CMeN(Me)$_2$ substituted phenyl ring [48]. Enantiomers of **16** each show a triplet in the ^{31}P NMR spectrum at $\delta_P = -121.95$ ($J_{PH} = 200.5$ Hz). This was the first enantiomerically pure phenylphosphine derivative reported in the literature, and can be used as an interesting synthon with broad applicability in the preparation of chiral P, N ligands by structural variation at the reactive PH$_2$ group. The authors demonstrated the use of such a ligand in assymetric catalysis. In the 3,5-dichlorophenyl phosphine [49] **17**, the introduction of the heavy chlorine atoms results in higher melting point compared to the phenylphosphine **1**; **17** is a colorless solid at room temperature.



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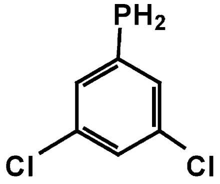

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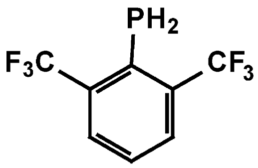

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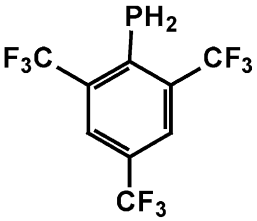

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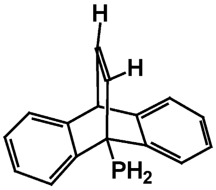
An interesting aryl phosphine 2,6-(CF$_3$)$_2$C$_6$H$_3$PH$_2$ [50] **18** was prepared by Bertrand and co-workers as a liquid (bp 31 °C/0.5 Torr). Subsequent deprotonation of this fluoro derivative yielded the first primary phosphanide anion [ArfPH]$^-$, stabilized by the bulky electron-withdrawing 2,6-bis(trifluoromethyl)phenyl group [51]. A similar phosphine, 2,4,6-(CF$_3$)$_3$C$_6$H$_2$PH$_2$ **19**, has been obtained as a low boiling point liquid [52,53].

2.1.2. *Alkyl phosphines*

The rare air-stable mono-primary phosphines with alkyl substituents include the nitrogen-containing cationic species of the general type [R$_3$N(CH$_2$)$_m$PH$_2$]$^+$I$^-$. Those are obtained by a selective *N*-quaternization of the corresponding primary phosphines [54]. The water solubility of these species with iodine anion decreases with increasing chain length of R. Completely water soluble hydrochlorides of formula [HR$_2$N(CH$_2$)$_m$PH$_2$]$^+$Cl$^-$ ($m = 2, 3$) were also prepared [54]. In our group, work has focused on “user-friendly” primary phosphines and arsines with alkyl substituents, whose inertness towards air could be enhanced by the introduction of bulky substituents, assuring a highly effective kinetic stabilization of these usually atmosphere-sensitive compounds. Such kinetic stabilization allowed us to obtain a new class of compounds with a rigid framework of organic substituents based on the barellene skeleton. The bulky barellene intermediates used for this purpose can be easily obtained by a high temperature Diels–Alder addition of the selected dienophile to the 9-bromoanthracene and subsequent functionalization with a PH$_2$ group [55]. All the barellene-derived primary phosphines **20** [56], **21** [57], **22** [58] and **23** [59] are colorless or slightly yellowish crystalline solids, with unusually high melting points.



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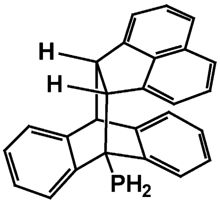

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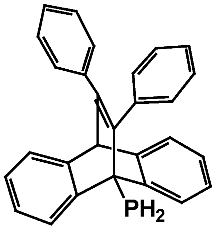

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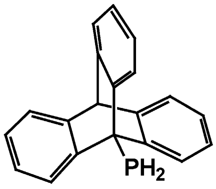

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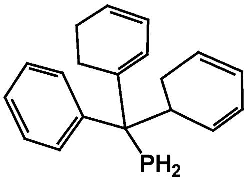

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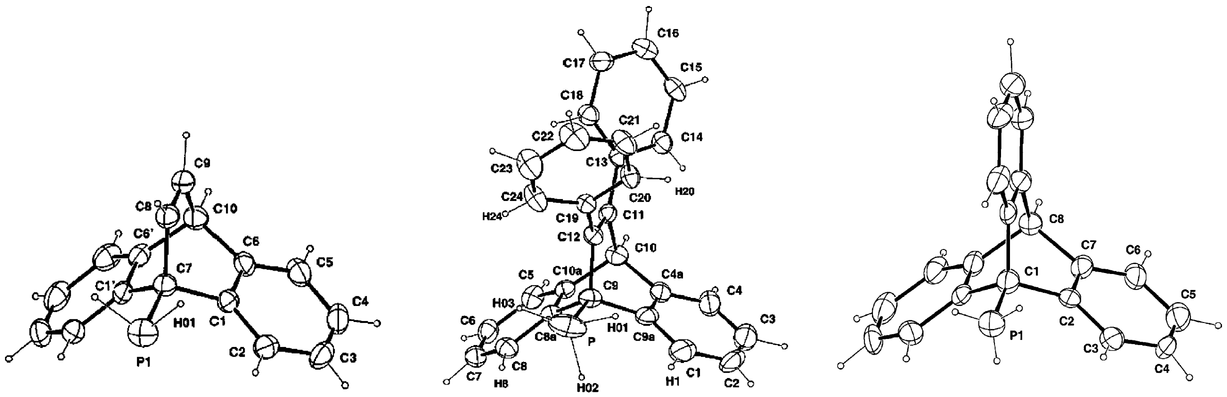
All four phosphines (**20–23**) show an unusual degree of air-stability. For example, crystals of diphenyldibenzobarellene phosphine DpdbbPH$_2$ **22** did not show any trace of oxidation after being stored at room temperature in air for more than 2 years. It is interesting to compare the stability of a series of primary phosphines with bulky substituents of increasing size with the trends of increasing melting points. As recently discussed [60], we believe that the extremely high stability of the triptycyl derivative of PH$_2$ **23** is mostly due to the particular role that the two sp^3 carbons play in the triptycene skeleton (Fig. 1). This bridge position lies on the symmetry axis of the triptycene and is protected by the adjacent protons of three symmetrical phenylene rings. Such a conformation ensures a noticeable steric hindrance of the substituent attached to this particular position and is the origin of this "cage protection" effect. The average distance between the three frontal phenylene protons is about 4.5 Å, a distance that is derived from crystal structures of different triptycene derivatives [60]. This is rather short relative to the size of the dioxygen molecules that are likely to approach the very reactive E–H bond, and could explain a high stability towards air and moisture. It is also interesting to compare the protecting ability of the triptycene moiety to the very similar triphenylmethyl (trityl) group [61], which has been used to stabilize a number of previously unisolable compounds. The trityl moiety possesses similar characteristics; although it is not as symmetric as triptycene, the C–E bond lies on the "pseudo" three-fold axis and is surrounded by three phenyl rings. In the trityl unit the average distance between the three frontal phenylene protons (4.4 Å) is also very close to that observed in the triptycene moiety. In order to explain the differences in the stabilizing "cage effect" between triptycyl and trityl groups, the shortest distance between the bridgehead carbon in triptycene (or analogous methyl carbon in the trityl unit) and the plane containing the three frontal phenylene hydrogens of the triptycyl unit (respectively, the three frontal hydrogens of the trityl group) has been estimated on the basis of the crystal structures of the various triptycene and trityl derivatives. In trityl, this distance is ca. 0.35 Å, while in the triptycyl fragment it is noticeably longer (ca. 0.60 Å). This difference in the "cage" dimension is probably responsible for the more pronounced stabilizing effect of the triptycyl moiety. For example, TrtPH$_2$ **24** was isolated [61] as a moderately stable solid (mp 76 °C) while TriptPH$_2$ **23** is a crystalline, highly air- and moisture-stable compound (mp 222 °C). Melting points of



(a) (b) (c)

Fig. 1. Perspective view of the 9-dibenzobarrelenephosphine **20** (a), 9-diphenyldibenzobarrelenephosphine **22** (b) and 9-tribenzo-barrelenephosphine **23** (c) (triptycylphosphine) with the atom numbering. Ellipsoids are represented with 40% probability level.

Table 2
Melting points of selected mono-primary phosphines

Primary phosphine	MW	mp (°C)	Compound no.	Reference
$PhPH_2$[a]	110	–[b]	**1**	[12]
$TrtPH_2$	276	76	**24**	[61]
$AnthPH_2$	210	88	**15**	[47]
Mes^*PH_2	278	114	**3**	[13]
$DbbPH_2$	236	108	**20**	[56]
$DpdbbPH_2$	388	141	**22**	[58]
$DimetPH_2$	360	213	**4**	[15]
$ArtippPH_2$	458	215–218	**14**	[8]
$TriptPH_2$	286	222	**23**	[59]
$AndbbPH_2$	360	240	**21**	[57]

[a] At room temperature exists in liquid phase.
[b] bp: 154–157 °C.

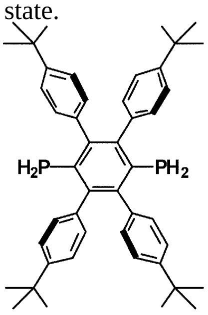
some selected triptycene derivatives were previously reported [60].

The majority of the triptycene-based molecules with bridgehead substituents melt above 200 °C. Together with a high rigidity, the "cage effect" is another important factor that can explain this unusual property of the various triptycene derivatives. The tandem influence of the rigidity and "cage" protection on the melting point is nicely illustrated by the trend observed in the increase of the melting point of primary phosphines (Table 2). The molecular skeletons of the $DbbPH_2$ **20** and the $DpdbbPH_2$ **22** do not allow a "cage" protection provided in **21** and **23**; moreover, both compounds exhibit a higher degree of flexibility than the corresponding triptycylphospine **23**. This is directly reflected by their melting points: 108 °C for **20**, 141 °C for **22** and 222 °C for **23**, respectively (Table 2).

2.2. Free bis and higher primary phosphines

2.2.1. Aryl phosphines

Protasiewicz and co-workers have reported a bisprimary phosphine **25** based on a tetraarylphenyl ligand of the form 2,3,5,6-Arx_4C_6 (Arx = *p*-*tert*-butylphenyl) which was investigated as a sterically demanding substituent for the protection of the two *p*-phenylene-bridged phosphorus centers [62]. This aryl phosphine was obtained as a white crystalline material, which is only very slightly air-sensitive and can be handled for short periods of time in air in the solid state.



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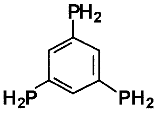

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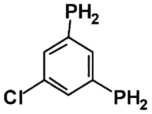

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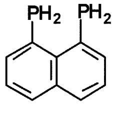

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Other characterized *n*-primary free aryl phosphines include *n*-benzophosphines: benzene-1,3,5-triyltrisphosphine ($C_6H_3(PH_2)_3$) **26** and the 5-chloro-1,3-phenylenebisphosphine **27** [49].

Compounds **26** and **27** are liquids under standard conditions. The substitution of a primary phosphine with a Cl atom or the organo group has a net influence on the solid–liquid equilibrium frontier, which is shifted towards solid state at room temperature. Thus, $C_6H_3(PH_2)_3$ and $C_6H_2Cl(PH_2)_2$ are liquids, but $C_6HCl_2PH_2$ **17** is a solid with a low melting point (21 °C). Structural characteristics obtained from crystal structures of **27** and **17**, show that the H-bonding between these primary aryl phosphines is extremely weak, and can have only a very minor influence on its supramolecular chemistry. The spatial arrangement of the two neighboring molecules in the crystal structure (Fig. 2) indicates that no significant interactions are detected in any of these derivatives. For example, in **27**, the P–P distance between two phosphorus sites of closest molecules is 4.2 Å with a 2.9 Å distance between H of the PH_2 group and other P atom, which exclude any H bonding to phosphorus. The same observation applies also for all the benzobarrelene phosphines crystal structures, but in this case the steric effects are in part responsible for rather large separation of the neighboring molecules. Reiter et al. have also very recently reported the synthesis of 1,8-diphosphinenaphthalene **28** [63], obtained as a colorless crystalline solid (mp 82 °C). In the crystal, the packing of the molecules of **28** was shown to not be governed by intermolecular hydrogen bonds.

2.2.2. Alkyl phosphines

A highly symmetric alkyl primary bisphosphine **29** was obtained by Schmutzler and co-workers, as a product of a [4 + 4] addition of two anthracenyl–PH_2 units under an irradiation with a Hg lamp [47]. This compound is air-stable and crystallizes in monoclinic space group $P2_1/c$. The CPH angles in the solid state were determined by X-ray crystallography to be 98(2)° and 97(2)°, respectively. Additionally, the crystal structure reveals the presence of only two PH_2 rotamers, which is in accordance with the expected, low energy

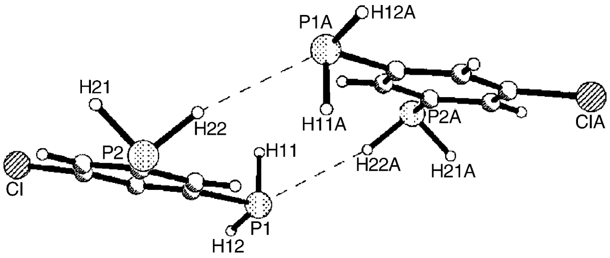
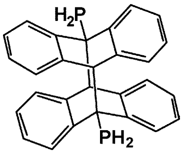


Fig. 2. A pair of symmetrical molecules of $C_6H_3Cl(PH_2)_2$ (**27**). The P–P contacts between the dimers (4.2 Å) are too long for significant H-bonding. Reprinted with permission from Ref. [49]. © 2002 Wiley-VCH Verlag.

barrier to rotation of the PH_2 units around the P–C bond (see Section 2.6).



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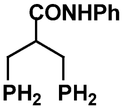
Katti et al. have successfully synthesized a number of new phosphorus derivatives with unusual oxidative stability, such as amide-, thioether- and carboxylate-functionalized primary bisphosphines. In a recent review [1], molecular structure, properties and applications of these primary bis phosphines are discussed as well as the utility of carboxylate-functionalized primary phosphines for incorporation onto peptides and their potential applications in catalysis and biomedicine.



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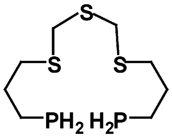

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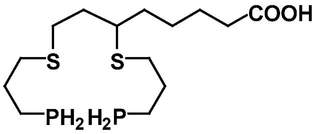

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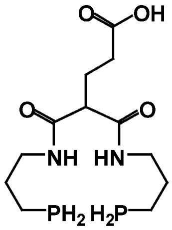

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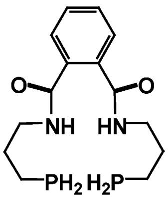

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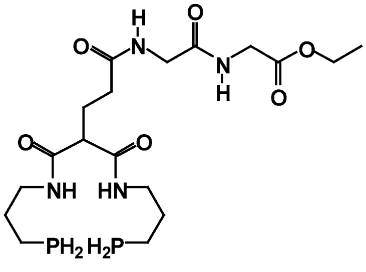

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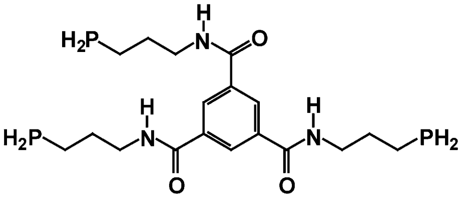

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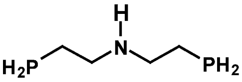
All the phosphines **30–36** are air-stable solids (unfortunately, no melting points were reported), except for **31**, obtained as colorless oil, which even in the liquid state, shows a good oxidative stability. Interestingly, **36** is one of the first examples of a primary phosphine functionalized with a peptide chain. This may be a useful synthon in engineering metal binding sites with specific biological functions. In this dipeptide conjugate, free PH_2 units are available for direct complexation to catalytically or biologically useful metals. Primary bis(phosphinoethyl)amines $RN–(CH_2–CH_2–PH_2)_2$ (R = H, *n*Bu, *p*-Tol) **37–39** obtained by alkylation of PH_3 are another subclass of bis primary phosphines [64]. These substances are obtained as high boiling point liquids, further used to complex molybdenum carbonyl species (see Section 2.4.3). Unfortunately, no specific information is provided about their oxidative stability.



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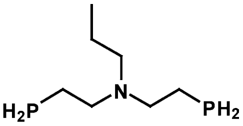

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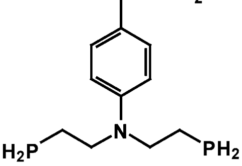
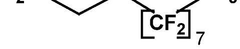


39

In the quest for a fluorous biphasic catalyst, Gladysz and co-workers reported the synthesis and characterization of a few primary phosphines with fluoro "pony tails" [65]. Fluorinated chains of the general formula $H_2P\text{-}(CH_2)_n(CF_2)_7CF_3$ were obtained by reactions of corresponding iodides and $LiPH_2$. The number of alkyl spacers ($-CH_2-$) seems to correlate with thermal and air-stability of these phosphines. Compounds **40** and **41**, which contain two and three CH_2 groups, respectively, between the PH_2 unit and the fluorinated chain, are high-boiling liquids. Compound **42** with a fourth CH_2 group is reported as a white solid with melting point close to RT.



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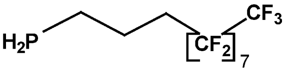

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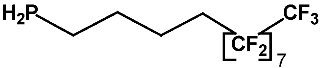

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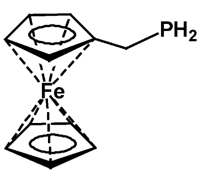
Compounds analogous to **26** (see previous paragraph) with alkyl spacers (up to three $-CH_2-$ groups) **43** have also been reported [66]. These trisarylphosphines were prepared by reduction of 1,3,5-tris[(diethoxyphosphinyl)alkyl]benzenes.

43 containing one CH_2 spacer ($n = 1$) is so unstable that it decomposes almost immediately to 3,5-bis(phosphinylmethyl)toluene and PH_3. Derivatives of **43** with two to four methylene groups are very hygroscopic, colorless liquids. Inert atmosphere techniques are required to handle these compounds.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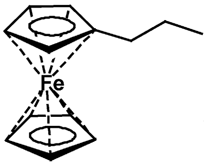
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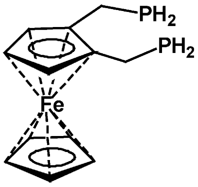
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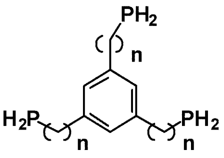
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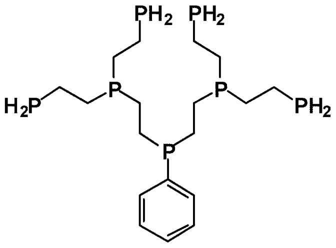
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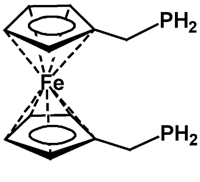
Despite their high air-sensitivity, interesting examples of liquid primary phosphines dendrimers, such as **44**, have been reported by Miedaner et al. [67]. The metallated octopus-like structures obtained by reaction of these dendrimers with $[Pd(CH_3CN)_4](BF_4)_2$ were observed to catalyze the electrochemical reduction of CO_2 to CO.

2.3. *Other free primary phosphines*

2.3.1. *Primary phosphines linked to ferroocenes*

Unexpected thermal stability was reported by Henderson and co-workers, for two mono-primary phosphines **45** and **46** with the PH_2 group linked to a ferrocenyl moiety via one or two CH_2 spacers [2,68,69]. Samples of **46** have been reported to remain stable in air for about 2 years with no sign of degradation, suggesting complete air-stability. The solution stability was not investigated in details by the authors, but also appeared to be good. Interestingly, the air-stability of this compound cannot be explained by steric factors, such as those observed in dibenzobarrelene phosphines or in sterically encumbered aryl phosphines, because the ferrocenylmethyl fragment is not extremely bulky. The spatial arrangement of the PH_2 unit, established on the basis of the X-ray structure, indicates that the phosphine function is oriented away from the ferrocenyl group, which rules out the possibility of any type of stabilizing interaction with the iron. Therefore, the authors state that the stability of these species is not fully understood and speculate that the stabilizing effect might be related to the kinetic stabilization due to the presence of the redox-active ferrocene group. This effect was also noticed to be proportional to the number of the CH_2 spacers introduced between the ferrocene moiety and the PH_2 group.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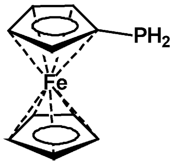
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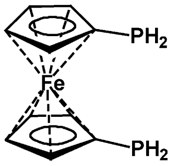
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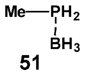
The extraordinary oxidative stability observed in the case of the ferrocene primary mono-phosphines also extends to the analogous bisphosphine species, where two PH_2 group are attached to ferrocene molecule via the alkyl spacers [2,70]. The 1,2-bisphosphine **47** is stable in air for several months, and the $1,1'$-isomer **48** for several weeks. Longer exposure of this latter compound leads to some degradation, but the residual phosphine can be easily repurified by flash column chromatography on silica gel. Their air-stability is strongly enhanced compared to the previously synthesized $FcPH_2$ [71] **49** and $Fc(PH_2)_2$ **50** [72–74]. Investigation of the oxidative process showed that $FcPH_2$ **49** is completely oxidized in solid form within 3 days to a mixture of primary phosphine oxide $[RP(O)H_2]$ and phosphinic acid $[RP(O)(OH)H]$. Moreover, immediate oxidation occurs for this compound in solution. $Fc(PH_2)_2$ **50** is less reactive towards air, but was also oxidized by air over a period of several days. These results confirm that the introduction of the alkyl spacers between PH_2 unit and ferrocene improves the air-sensitivity of these phosphines, in a manner similar to that observed in compounds **40**–**42**.

2.4. *Complexes of primary phosphines*

While there is an extensive literature that deals with the coordination chemistry of tertiary and secondary phosphines, the transition-metal chemistry of primary phosphines is less well known. Fundamental differences in the steric and electronic structure of the tertiary (or secondary) and primary phosphines are expected to influence the intrinsic properties of the corresponding ligands. For example, the basicity of the phosphorus lone pair is modified by the substitution of an alkyl or aryl group on phosphorus with a hydrogen atom. The decrease in basicity is believed to result from the distinct geometry of the PH_2 unit, which differs also from its PR_3 congener in that it has a smaller cone angle: in primary phosphines bond angles are nearly 90°, while in many of their tertiary homologues they exceed 100°. The narrower angles in the primary phosphines result in increased s character in the phosphorus lone pair orbital [19,75]. Also, systematic investigations of the coordination behavior of primary phosphines have encountered some difficulties, which are mainly due to the facility with which the P–H bonds undergo a metal-mediated cleavage to form phosphido or phosphinidene ligands. In this section, a brief overview of the primary phosphine complexes with boron and transition metals is presented, again with emphasis on the stability and robustness of the representatives of this class of compounds. Mention must also be made of another class of phosphorus compounds, namely the transition metal substituted phosphines, which although bearing similar appellation, exhibit discernible structural characteristics that separate them from the R–PH_2–M type primary phosphines complexes. As it extends well over the scope of this short review, this parent class of compounds where the isolate PH_2 (or AsH_2) units serve as ligands is excluded from the following sections. Another class of compounds, which is not strictly within the scope of this review, and were omitted here, are the alkali metal derivatives of primary phosphines, which are very useful transfer reagents (see, for example, Ref. [76]).

2.4.1. Complexes with boron

Although the phosphine–boranes tend to be oxidatively unstable compounds that decompose over time or upon heating, there has been an increased interest for such species in the past years. This new boron–phosphine chemistry was initiated by the simplest complexes of R–PH_2 with BH_3, which can be easily obtained by reaction of $BH_3{\cdot}SMe_2$ with the corresponding primary phosphines. Such compounds are known with phenyl or methyl phosphines [77]. The BH_3 complex with phenylphosphine **52** is a colorless solid with a low melting point (50 °C) while its methyl analogue **51** is a colorless liquid at RT. When the more sterically demanding PH_2Mes is complexed with BH_3, colorless needles of **53** with a mp of 83 °C are obtained, which can be easily recrystallized from a THF/petroleum ether mixture [75].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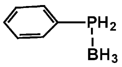
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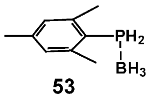
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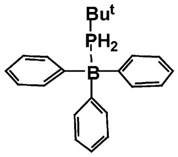
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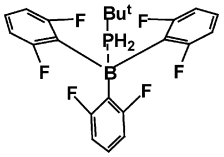
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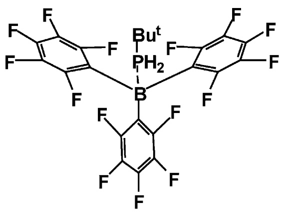
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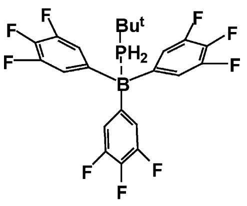
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The first single-crystal X-ray structure of a primary phosphine–borane adducts was reported by Dorn et al. [78] for **52**. The same paper reported the synthesis of $^{i}BuPH_2{\cdot}BH_3$, which was obtained as colorless oil. The $PhPH_2{\cdot}BH_3$ crystallizes in the monoclinic system within $P2_1/c$ space group, with a staggered geometry and a P–B bond length of 1.924(4) Å. The P–H bond length is 1.33(4) Å and the closest intermolecular contacts (2.47(6) Å) were found between two hydrogen atoms connected to phosphorus in two "head-to-head" oriented molecules (Fig. 3). However, these contacts might be underestimated due to the systematic errors in determining the positions of P–H atoms, which were located and refined in order to determine the P–H bond length. Two molecules form a centrosymmetric dimer with very weak intermolecular H···H interactions.

Improved stability is provided in the boron–phosphine complexes where the boron atom is surrounded by bulky ligands. This is clearly evidenced by the complexes of *tert*-butylphosphine with triphenylboron **54**, tris(2,6-difluorophenyl)boron **55**, tris(pentafluoropheny1)boron **56** and tris(3,4,5-trifluorophenyl)boron **57**, whose crystal structures have been reported [79].

The strength of the interaction of the latter triarylboron compounds with phosphine increases with the number and position of the fluorine atoms attached to the phenyl ring, the *ortho* position being the most important. For example, tris(pentafluorophenyl)boron is a much stronger acceptor than tris(2,6-difluorophenyl)boron, and the latter is a stronger acceptor than the tris(3,4,5-trifluorophenyl)boron. This was suggested to be due in part to the extent of π-system overlap with the vacant boron p-orbital, which is clearly dependent upon the amount of the substitution with electronegative fluorine atoms. Less overlap is expected from the depleted π-system with more electronegative fluorine atoms in the vicinity of the boron atom, as in the case of 2,6-trifluorophenyl or pentafluorophenyl ligands, which encourages a stronger interaction with phosphine.

2.4.2. Complexes with vanadium, niobium and tantalum

Ho et al. reported a cationic, crystalline vanadium complex $[Cp_2V(PH_2Ph)_2][BPh_4]$ **58** [80], obtained by reaction

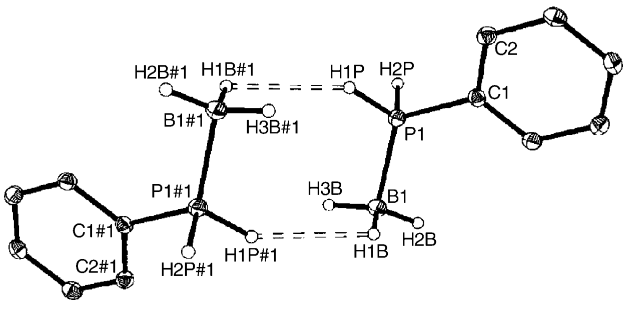
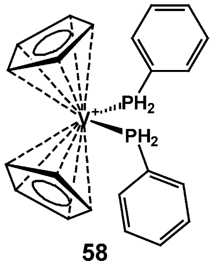


Fig. 3. A pair of symmetrical molecules of $PhPH_2{\cdot}BH_3$ (**52**) showing weak intermolecular H···H interactions. The H···H distances are ca. 2.47(6) Å. Reprinted with permission from Ref. [78]. © 2000 American Chemical Society.

of $[Cp_2V][BPh_4]$ with $PhPH_2$. The crystal structure shows a pseudotetrahedral coordination sphere for V, which is composed of two Cp ligands and two P atoms derived from two coordinated PH_2Ph ligands. The V–P distances are 2.391(2) and 2.418(2) Å, slightly shorter than in the related $Cp_2V((PPh)_2)$ (2.538(4) and 2.541(4) Å), consistent with the cationic nature of this compound. The P–V–P angle is 83.52(8)°, typical of disubstituted metallocenes.



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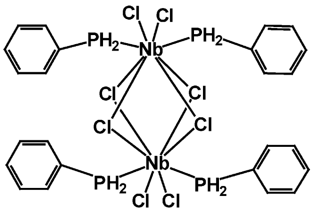

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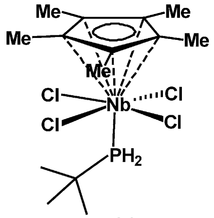


60

Niobium complexes octachlorotetrakis(cyclohexylphosphine)-diniobium(IV) and octachlorotetrakis(phenylphosphine)-diniobium(IV) **59** were recently prepared [28] by the reaction of niobium pentachloride with excess cyclohexylphosphine or phenylphosphine in dichloromethane. The one-electron reduction of niobium(V) to niobium(IV) yielded brown-red and dark red crystalline solids, respectively. Both compounds have chloride-bridged structures with Nb–P bond distances of 2.613(1) and 2.617(1) Å for the cyclohexylphosphine complex and 2.633(2) and 2.634(2) Å for the phenylphosphine complex. P–Nb–P angles are 113.0(1)° and 114.69(4)°, respectively. As a side product of the same reaction, an air-sensitive, purple precipitate was isolated, which was identified as $[C_6H_{11}PH_3]_2[NbCl_6]$. The presence of cyclohexylphosphonium ions in this intensely colored complex was supported by P–H stretches at 2443 and 2404 cm^{-1} in the IR spectrum, compared to a P–H stretch at 2285 cm^{-1} in neat cyclohexylphosphine. The hydrogen atom in the ionic complex has been suggested by the authors to originate from the cyclohexylphosphine. Such a hydrogen source is not surprising, in view of the relatively low phosphorus–hydrogen bond strength (70.9 kcal mol^{-1} in PH_3) [81].

Tetrachlorometallocene complexes of primary phosphines, examplified by **60**, were synthesized in high yields by Blaurock and Hey-Hawkins [82] by the reaction of equimolar amounts of RPH_2 and corresponding $[Cp^*MCl_4]$ ($R = {}^tBu$, Ad, Cy, Ph, Mes; M = Ta, Nb) in toluene. The yellow or red crystals thus obtained are air- and moisture-sensitive and decompose easily in ethers with liberation of the primary phosphine. This is believed to result from replacement of the phosphine by the coordinating solvent. In all these isostructural complexes, the crystal structure reveals a pseudo-octahedral geometry for the metal, with the phosphine ligand located *trans* to the Cp* ligand. M–P bonds are rather long (Ta–P, 2.64–2.70 Å and Nb–P, 2.64–2.69 Å, e.g., $[Cp^*TaCl_4(MesPH_2)]$ 2.704(1) Å; $[Cp^*NbCl_4(MesPH_2)]$ 2.691(1) Å) compared to the M–P bond lengths of other known niobium and tantalum phosphine complexes (2.59–2.67 Å), where the metal center is coordinated with tertiary phosphine. This may be due to the steric influence of the chlorine ligands or the *trans* effect of the Cp* ligand. According to the authors, the M–P–C bond angles are large (ca. 121.8–130.6°, e.g., $[Cp^*TaCl_4(MesPH_2)]$ 126.8(1)°; $[Cp^*NbCl_4(MesPH_2)]$ 126.8(1)°) due to the greater steric demand of the metallocene group compared to two hydrogen atoms of the PH_2 group in the free phosphine.

In the crystal structure of the niobium complex **60** [82], intermolecular H-bonding from H(P) to chlorine atom (H···Cl, 2.90 Å) was observed (Fig. 4). Such weak interaction is probably responsible for the formation of polymeric layers. A similar tantalum complex containing the bulky $PH_2(2,4,6\text{-}{}^iPr_3C_6H_2)$ ligand was also reported by the same group [83] to form yellow crystals (mp 147 °C), which are only slightly air-sensitive, but are quickly hydrolysed. The complex crystallizes in triclinic space group $P\bar{1}$ and contains two molecules per unit cell with a C–P distance of 1.841(8) Å. The bond lengths and angles for the PH_2 units are typical (P–H, 1.42 Å; C–P–H, 105.9°; H–P–H, 106.2°). The Ta atom has a pseudo-octahedral geometry, with the RPH_2 ligand *trans* to the Cl ligand, and the Ta–P distance is 2.710(2) Å.

2.4.3. Complexes with chromium, molybdenum and tungsten

Tungsten complexes, such as tungsten pentacarbonyl, have been used as useful substrates for the stabilization of alkyl primary phosphines that have not previously been observed in the free state [84] as well as primary alkynylphosphines and allenylphosphines that are otherwise highly unstable [85]. Complexes of primary phosphines with Mo, such as **61**, were prepared by a direct complexation of RPH_2 (R = Cy, $2,4,6\text{-}{}^iPr_3C_6H_2$) with $Cp'MoCl_4(CH_3CN)$ [86]. The adducts were obtained as brown crystals which melt with decomposition at 134.5 and 139 °C, respectively. For both compounds, the crystal structure reveals pseudo-octahedral geometry about the Mo center, with the RPH_2 unit located *trans* to the Cp′ ligand. The Mo–P bond distances in these 17-electron species are ca. 2.554(1) and 2.617(1) Å. EPR spectra of both complexes are consistent with a pentavalent Mo(V) of spin 1/2 and the EPR spectrum of $[(2,4,6\text{-}{}^iPr_3C_6H_2)Cp'MoCl_4]$ at RT and in frozen solution allowed an estimation of the degree of hybridization ($n^2 = 0.8$) close to that expected for tetrahedrally coordinated P atom ($n^2 = 0.75$) [86]. Dimeric $Mo_2Cl_4(PH_2Ph)_4$ was synthesized by Cotton et al. [87] but no crystal structure was reported for this compound.

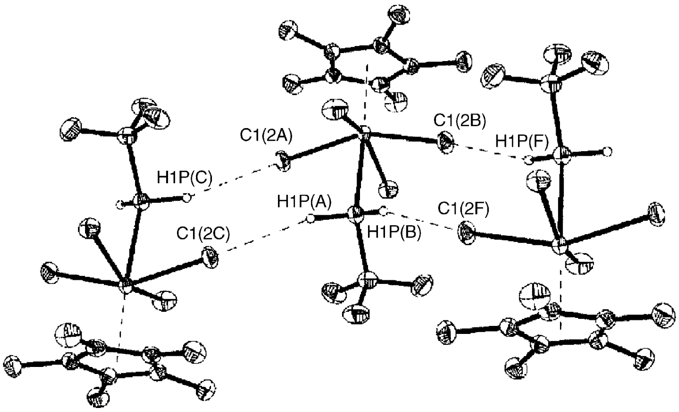
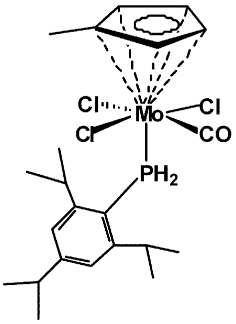


Fig. 4. Neighboring molecules of [Cp*MCl$_4$(^{t}BuPH$_2$)] **60**. An intermolecular bonding between H (PH$_2$) and Cl atoms with H···Cl distance of 2.90 Å is observed. Reprinted with permission from Ref. [82]. © 2002 Wiley-VCH Verlag.



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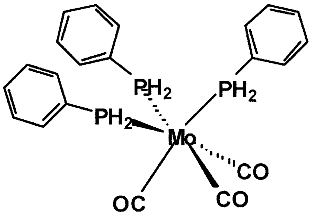

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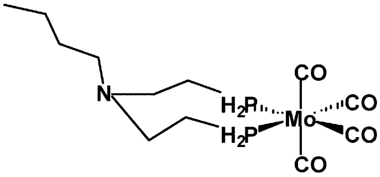

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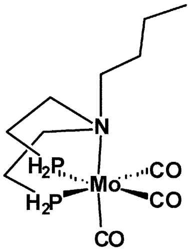

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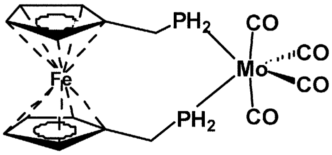

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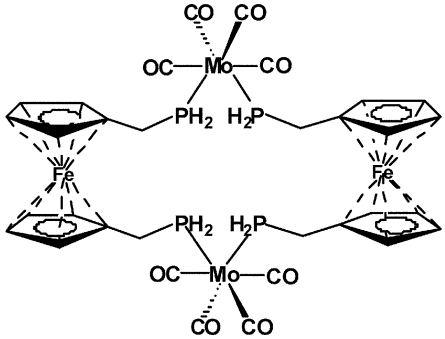

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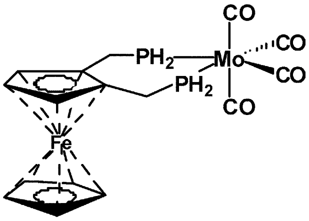

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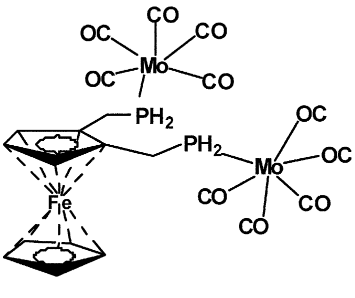

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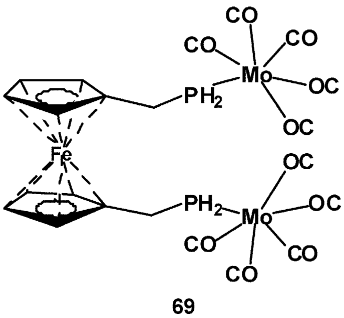


69

Harlan et al. [88] reported the synthesis of new tungsten–primary phosphine complexes by reduction of high oxidation state tungsten complexes. Reaction of $[Cp^{*}WCl_4]_2$ with two equivalent of Ph(H)PLi gave the monomeric phosphine adduct $[(Cp^{*}WCl_4)(H_2PPh)]$ in low yield. This product was suggested to result from the disproportionation of Ph(H)PLi into Li_2PPh and $PhPH_2$. For both compounds, paramagnetic behavior was observed in solution. These 17-electron species form dark, green-brown crystals that are stable for short periods of time in air. $[(Cp^{*}WCl_4)(H_2PPh)]$ crystallizes in the monoclinic $P2_1/c$ space group with four molecules in the unit cell, with a W–P distance of 2.569(5) Å. The phosphinic protons were not located in the X-ray structure, but the presence of unaffected PH_2 units was nevertheless confirmed by a characteristic stretch at 2300 cm^{-1} in the IR spectrum. *trans*-$WCl_4(H_2P\text{-}{}^{t}Bu)_2$ was obtained as red crystals (monoclinic $C2$ space group) from the reaction of WCl_6 with excess ${}^{t}BuPH_2$, via reduction of W(VI) by the primary phosphine. It is worth noting that the space group $C2$ was refined later by Marsh and Spek to the correct $C2/m$ group [89].

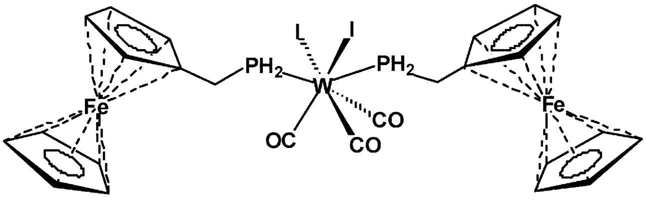
In 1993, Schmutzler and co-workers reported a series of complexes obtained from the reactions of adamantyl phosphine with metal carbonyl fragments of type $M(CO)_6$ (M = Cr, Mo, W), $Fe_2(CO)_9$ or $Ni(CO)_4$ [90]. All these compounds are solids at RT (except for the $AdPH_2Ni(CO)_3$, which was obtained as a colorless oil that easily crystallized at −18 °C), and were characterized as “rather unreactive”. The group VI complexes formed colorless crystals characterized by high melting points (100–146 °C). Complex with Fe is a intensely colored orange-brown solid with lower melting point (92 °C). It is worth noting that the complex with Fe formed a variety of cluster compounds, none of which contained a primary phosphine ligand. All of these solids are stable in air for several hours and can be handled in an open air atmosphere. A series of paramagnetic complexes $Cp^{\circ}MoCl_4(PH_2R)$ (where R = ${}^{t}Bu$, Ad, Cy, Ph, Mes and Tipp) with melting points varying from 149 to 179 °C has been reported by Hey-Hawkins and co-workers [91]. These compounds are rare examples of metal(V) complexes with primary phosphines, and were prepared to prevent the reduction of Mo(V) by employing a primary phosphine instead of the highly reducing lithium reagents for the introduction of a P-functionalized ligand.

Bisprimary bis(phosphinoethyl)amine $n\text{-}BuN(CH_2CH_2PH_2)_2$ can be complexed by molybdenum yielding moderately stable species [64]. The resulting complex **63** crystallizes in the orthorhombic space group *Pbca* ($Z = 8$) with P–Mo distances of 2.510(2) and 2.515(2) Å. An interesting behavior of the amino-tail is highlighted in the “scorpionate” complex **64**; while in **63** the nitrogen atom is far away from the metal center, in **64** N atom displaces one of the CO ligands and a compact cage-structure is formed. Complexes of $PhPH_2$ coordinated to Mo, Cr or W have been reported by Campbell et al. [92]. Di- and tri-substituted complexes *fac*-$[M(CO)_3L_3]$ (M = Mo or W; L = $PPhH_2$), *cis*-$[M(CO)_4L_2]$ (M = Cr, Mo or W; L = $PPhH_2$) were synthesized together with a diprimary phosphine complex *cis*-$[Mo(CO)_4\{o\text{-}C_6H_4(PH_2)_2\}]$. In *fac*-$[Mo(CO)_3(PPhH_2)_3]$, a neutral molecule is found in the asymmetric unit, with the primary phosphine ligands in a *fac* arrangement giving a distorted octahedral geometry at Mo. The P–Mo bond distances lie in the range 2.493(3)–2.501(3) Å and the *cis* angles around the metal center are 86.78(9)–92.9(3)°. The crystal structures of the disubstituted species $[Mo(CO)_4(PPhH_2)_2]$ show a *cis*-disubstituted arrangement at the metal center, giving a distorted octahedral geometry and confirming the structure deduced spectroscopically in solution. The P–Mo distances are both 2.508(3) Å and the P–Mo–P angle 87.9(1)°. The integrity of the PH_2 units was confirmed by X-ray crystallography, proving that primary phosphines behave as neutral two-electron donors to Group 6 metal carbonyls. From the comparison of the crystallographic data, the authors concluded that the Mo–P bond lengths are virtually insensitive to the degree of substitution at Mo, and that different cone angles of the phosphines have little effect on the geometry about molybdenum. A prop-2-enylphosphine complex of Cr with four carbonyl ligands $Cr(CO)_4H_2PCHMe(CPHCH_2)Me$ was also reported [93].

Monomeric and dimeric ferrocenylphosphines adducts with molybdenum were obtained as crystalline, slightly yellowish materials with moderately elevated melting points (129–150 °C) [2]. They were prepared by reaction of the primary phosphines with molybdenum carbonyl–piperidine complexes. Monomeric **65** and **67** were obtained from $[Mo(CO)_4(Pip)_2]$ and the corresponding ferrocenyl phosphines. Coordination of the phosphine resulted in a typical shift of the ${}^{31}P$ NMR signal from $\delta = -128$ in the free phosphine to $\delta = -79$ in the complex. The seven-membered ring formed in **67** adopts a boat conformation. Yellowish crystals of the dimer $[1,1'\text{-}Fc(CH_2PH_2)_2Mo(CO)_4]_2$ **66** were obtained as a minor product of the same reaction. The use of excess of the labile $[Mo(CO)_5(THF)]$ leads to two complexes, **68** and **69** (melting points 119–121 and 138–142 °C, respectively), which are air-stable for several months, and are easily prepared and handled. Interestingly, molybdenum derivatives **65**, **66** and **67** with four CO groups decompose on heating, whereas the derivatives **68** and **69** with five CO groups have clearly defined melting points.

The first known primary ferrocenylphosphine complex of tungsten(II) **70** [94] was reported by Hey-Hawkins et al. This compound crystallizes in the triclinic $P\bar{1}$ space group with two molecules per unit cell and an additional non-interacting, disordered molecule of THF. Compound **70** has a distorted capped octahedral structure, with *trans*-phosphine ligands and a carbonyl group that caps a triangular face formed by two carbonyl and one phosphine ligand. The P–W distances are 2.472(3) and 2.536(3) Å and the PH_2 unit in the vicinity of the carbonyl ligand shows a major deviation from the octahedral position, due to the steric influence of the ligand. The complex is described by the authors as a solid with mp

150 °C, which is stable in air for several months, but in solution it is air-sensitive and decomposes within 24 h.



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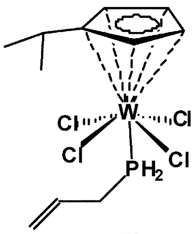

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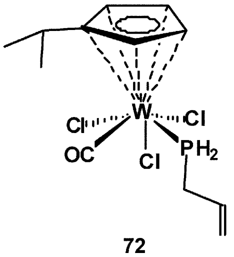


72

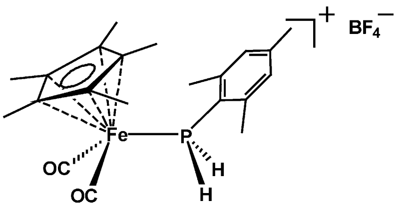
η^5-Cyclopentadienyltungsten complexes with vinyl- and allyl-phosphine ligands $PH_2(CH=CH_2)$ and $PH_2(CH_2CH=CH_2)$, such as **71**, were prepared by Morise et al. [95]. The bifunctionality of these primary phosphines is clearly demonstrated by their ability to act as ligands to transition metals by coordination through the phosphorus atom or the carbon–carbon double bond, or both. The complexes thus obtained show paramagnetic behavior in solution and are rather air-sensitive. The presence of unaffected PH bonds was confirmed by bands in the IR spectra assignable to the PH stretch in the range 2392–2396 cm^{-1}. The values for $\nu(P\text{–}H)$ are ca. 100 cm^{-1} lower than those for the corresponding uncoordinated primary phosphines. The crystal structure of **71** exhibits a distorted octahedral symmetry with the four chlorine atoms lying in the equatorial plane. The W–P distance is 2.554(2) Å and P–C bond is 1.77(1) Å. Reductive carbonylations of these tungsten(V) compounds to the tungsten(IV) species can be easily achieved by treatment with $[Fe_2(CO)_9]$ [96]. The crystal structure of $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(H_2PC_3H_5)(CO)]$ **72** shows that the phosphine ligand occupies an equatorial position and is *cis* to the carbonyl group, in contrast to the starting material $[W(\eta\text{-}C_5H_4{}^iPr)Cl_4(H_2PC_3H_5)]$ **71** where PH_2 occupies the axial position. The W atom has a significantly distorted octahedral coordination, with two *cis*-Cl ligands, a CO and a phosphine ligand in the pseudo-equatorial plane and with the Cp-ring centroid *trans* to the Cl ligand. The considerably shorter W–P distance (2.472(1) Å) compared to similar W–P complexes (2.55–2.57 Å) was partially attributed to the *trans* influence of the chlorine ligand.

2.4.4. Complexes with manganese

Neutral complexes of primary bisphosphines with manganese, ($[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$ and $[MnBr(CO)_3(PhPH_2)_2]$), were recently reported by Pope and Reid [97] from the reaction of $[MnX(CO)_5]$ (X = Cl, Br) with the respective phosphine in the correct stoichiometry. These neutral species are yellow or orange solids, which are stable in the solid state. This stability also extends to the solution state, where they appear to be quite stable unless exposed to oxygen. In addition, they are the first structurally characterized primary phosphine complexes of manganese. The structural analyses confirm the integrity of the coordinated PH_2 units and the same stereochemistry in the solution and solid states. The crystal structure of $[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$ shows the *fac*-octahedral arrangement predicted from the spectroscopic studies, with a chelating diphosphine. The Mn–P distances for $[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$ are 2.280(2) and 2.281(2) Å and for $[MnBr(CO)_3(PPhH_2)_2]$ they are 2.305(1) and 2.322(1) Å, respectively.

2.4.5. Complexes with iron, ruthenium and osmium

Cationic primary phosphine iron complexes such as **73** and **74** were used by Malisch et al. for hydrophosphination, yielding P-chiral functionalized phosphines [98–100].



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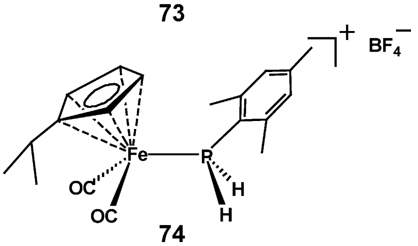

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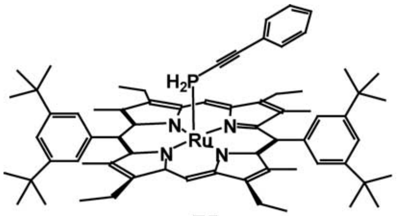
Complex **73** is a light beige crystalline material (mp 76 °C) and its congener **74** forms yellow crystals (mp 154 °C). One of the first primary phosphines to be complexed with osmium was reported by Schmutzler's group in 1992 [47] as an $AnthPH_2\text{–}Os_3(CO)_{11}(MeCN)$ solid adduct with mp 138–140 °C. Unfortunately, no crystal structure was reported for this compound. Phenylphosphine can be easily complexed by ruthenium and osmium chloride yielding *trans*-$[MCl_2(PhPH_2)_2]$ (M = Ru, Os) [101] via reaction of $RuCl_3\cdot 3H_2O$ or $[NH_4]_2[OsCl_6]$ with excess $PhPH_2$. Analogous bromine derivatives can be used for this latter reaction yelding *trans*-$[RuBr_2(PhPH_2)_4]$ and *trans*-$[OsBr_2(PhPH_2)_4]$ [102], in which the presence of the protons attached to phosphorus in PH_2 was confirmed by ^{31}P NMR and IR spectroscopy (PH band at 2340 cm^{-1}). Cyclic voltammetry reveals reversible $Os^{II/III}$ redox couple at easily accessible potentials, confirming that deprotonation of the PH_2 function does not occur on the cyclic voltammetry time-scale even in the more electropositive Os(III) species [102].

Crystalline osmium(II) complexes with $MesPH_2$ were obtained [103] from the reaction of mesitylphosphine with $OsHCl(CO)(PPh_3)$. Two species are of interest:

cationic $[OsCl(MesPH_2)(CO)_2(PPh_3)_2]ClO_4$, which was separated as a mixture of isomers (mp 173 °C), and neutral $OsHCl(MesPH_2)(CO)(PPh_3)_2$, which forms colorless crystals with a mp of 181 °C.

Very air-sensitive, primary alkynyl phosphine porphyrins were prepared by $AlHCl_2$ reduction of the corresponding alkynyl phosphonates in an attempt to find suitable building blocks for the construction of larger multiporphyrin systems [104]. Unfortunately, these primary phosphines are highly unstable and must be handled under an inert atmosphere. In solvents such as chloroform, the degradation of the compounds is observed within a few hours. While $PaPH_2$ [85] is complexed with Ru porphiryns, mono and bis phosphine adducts **75** and **76** are observed. NMR studies indicate that the bis-phosphine complex with ruthenium(II) porphyrins is more stable than the mono-phosphine complex, but in all cases the complexes could not be isolated and they degrade within hours at ambient temperatures when kept in solution. The IR spectrum of the complex $(PaPH_2)Ru(CO)$ (porphyrin) indicates weak σ-donor properties of the ligand.



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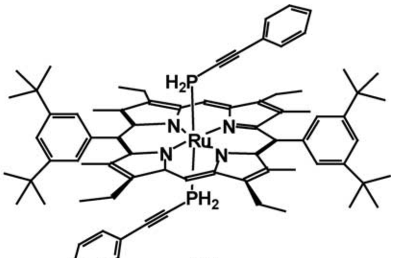

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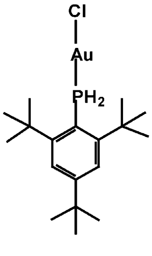
2.4.6. Complexes with nickel, palladium, copper, silver and gold

Interest in phosphine–gold complexes is in part related to their promising in vitro and in vivo antitumor properties [105]. Au–RPH_2 complexes were reported by Schmidbaur et al. [29], in which various primary phosphines were reacted with (CO)AuCl to give R–PH_2–AuCl (R = Mes, MesEt, Tipp, Mes*), exemplified by **77**. The stability of these products once again depends markedly on the robustness of the phosphine ligand. While the $MesPH_2$ complex decomposes at −20 °C, the other three complexes are all stable, crystalline solids at room temperature with melting points of 84–138 °C. Interestingly, the crystal structure of the Mes* complex, which crystallizes in the monoclinic system (space group $P2_1/n$, four molecules in the unit cell), shows a coplanar arrangment of the phenyl rings in the crystal packing. Molecular twins adopt a head-to-tail pairing of the P–Au–Cl groups with the closest distance between the two Au atoms being 3.440(1) Å. The P–Au distance is 2.242(2) Å and the PH bond distances are 1.350 and 1.368 Å, which is typical of this type of primary phosphine. Very recently, two phenylphosphine complexes $[Au(C_6F_5)(PhPH_2)]$ and $[Au(C_6F_5)_3(PhPH_2)]$ were prepared by reacting $[Au(C_6F_5)_x(THF)]$ ($x = 1$, 3) with an equimolar amount of $PhPH_2$ [106]. Both of these phosphino complexes are white solids, moderately air- and moisture-stable and soluble in chlorinated solvents and acetone. The gold(I) species is less stable in solution, and undergoes rapid autodeprotonation to yield C_6F_5H.

Ni, Pd, Cu and Ag complexes were prepared from mesitylphosphine and $Ni(COD)_2$, $[Pd(NCMe)_4][BF_4]_2$, $[Cu(NCMe)_4]PF_6$ and $AgBF_4$, respectively [75]. Subsequent reaction of these primary phosphine adducts with triphos or tetraphos led to derivatives $Ni(triphos)MesPH_2$, $[Cu(triphos)MesPH_2][PF_6]$, $[Ag(triphos)MesPH_2][BF_4]$ or $[M(tetraphos)MesPH_2][BF_4]_2$ exemplified by cationic **78**. All the complexes were obtained as white to yellow, solid, crystalline materials. The pale-green needles of the nickel complex are air-sensitive, while the remaining complexes are inert to air and water in both the solid and solution states, except for the Ag adduct with tripos, which slowly loses $MesPH_2$ in solution. $Ni(MesPH_2)_4$ **79** is tetrahedral in the solid state, with an average Ni–P bond length of 2.149 Å (2.140(8)–2.158(7) Å) and P–Ni–P angles ranging from 106.9(3)° to 111.3(2)°. Complex $[Cu(MesPH_2)_4][PF_6]$ shows distorted tetrahedral geometry with two sets of Cu–P distances close to 2.27 and 2.30 Å (2.269(2)–2.298(3) Å), and P–Cu–P angles range from 104.0(1)° to 116.5(1)°. The ^{31}P NMR suggests that the four phosphine ligands are equivalent in solution, so that the distortions observed in the solid state may be a consequence of crystal packing forces. Other homoleptic, highly air-sensitive copper adducts $[Cu(PH_2Ph)_4]^+$ [107], Cu-$[1,2(PH_2)_2C_6H_4]_2^+$ [108,109] and bridged [110] $Cu_2I_2(PhPH_2)_4$ are also known.



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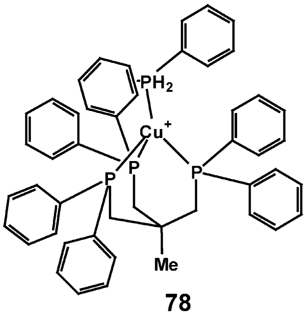
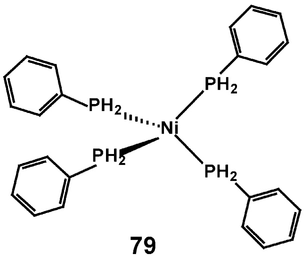


78



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2.4.7. Complexes with cobalt and rhodium

Rhodium and cobalt complexes Cp*$RhCl_2$(Mes*PH_2), Cp*$RhCl_2$(IsPH_2) and CpCoI_2(Mes*PH_2) were reported by Termaten et al. [111]. Cp*$RhCl_2$(Mes*PH_2) and Cp*$RhCl_2$(IsPH_2) are both crystalline materials with high melting points (red needles, mp >240 °C and orange crystals, mp >190 °C, respectively). CpCoI_2(Mes*PH_2) was obtained as a solid with relatively high melting point (>140 °C) in the form of a green-black precipitate. It was reported to be stable in the solid state but decomposed slowly in solution, which hampered its crystallization. The other known Co and Rh complexes are the sulfonoalkyl $Co[H_2PCH_2CH(CH_3)SMe]_3BF_4$ and $CoL_3\cdot CoCl_2$ where HL = $H_2PCH_2CH_2SH$, $H_2PCH_2CH(CH_3)SH$ [112].

2.5. ^{31}P NMR spectroscopy

The interpretation of NMR chemical shift values for phosphorus compounds involves several factors such as the distribution of electron density in the bonds between phosphorus and its substituents, the extent of phosphorus participation in bonding and the bond angles about the phosphorus. In the case of primary phosphines, the angles between C–P and P–H bonds are nearly constant. Some theoretical predictions of the ^{31}P NMR spectral data based on density functional theory (DFT) [113–115] or quantitative structure–property relationships (QSPR) method [116] have recently been reported.

In Table 3, we have compiled the ^{31}P NMR spectral data for free primary phosphines and their complexes discussed in this work. A characteristic NMR “fingerprint” for all the spectroscopically characterized free primary phosphines R–PH_2 involves a strongly negative ^{31}P chemical shift (−150 to −200 ppm) and a J_{PH} coupling constant close to 200 Hz. In many cases, when the primary phosphines are produced by the reduction of respective chlorophosphine, the corresponding ^{31}P NMR spectrum of the “crude” material contains a characteristic signal of the residual PH_3 at −238 ppm. This results from the reduced excess phosphorus trichloride remaining from the reaction of the precursor with PCl_3. While a relatively constant J_{PH} coupling near 200 Hz seems to be diagnostic for all free alkyl and aryl primary phopshines, this is not true for the ^{31}P chemical shift. An analysis of the NMR data shows that for the bulky phenyl substituted primary phosphines δ varies from −121.6 ppm in PhPH_2 to −158.2 ppm in TippPH_2. The bulky alkyl phosphines are characterized by chemical shifts that range from −156.0 ppm in TriptPH_2 to −143.6 in DbbPH_2. Here, the range of the chemical shifts is substantially smaller (∼12 ppm) and reflects the fact that in all these phosphines, the PH_2 group is connected to the same dibenzobarellene skeleton. Under oxidative degradation, signals with $\delta = -20.0$–0.0 and large J_{PH} coupling (450–500 Hz) are typically detected in the ^{31}P NMR spectrum. These are due to the presence of oxidation products RP(O)H_2 (see, for example, the oxidation products of Mes*PH_2–$J_{PH} = 490.7$ Hz, $\delta = -10.0$ [117] or 2,6-di-isopropylphenylphosphine, DipPH_2 $J_{PH} = 477$ Hz and $\delta = -14.6$ [45]).

When R–PH_2 undergoes complexation with a transition metal, an increase in the J_{PH}-coupling constant as well as in the ^{31}P chemical shifts are observed, consistent with primary phosphine coordination. This is related to the change in the hybridization of the P atom leading to more s character in the P–H bond [118]. Coordination to BH_3 results in a similar behavior. Literature data on a variety of phosphorus compounds show equally that electronegative substituents X on the P atom increase J_{PH} couplings, an effect rationalized by increased p character in the P–X bonds, which leads to increased s character in the P–H bonds. ^{31}P NMR data compiled here for the phosphine metal complexes are consistent with this trend. For example, in cationic species reported by Kourkine et al. [75], $[Pd(MesPH_2)_4][BF_4]_2$ and $[Pd(tetraphos)(MesPH_2)][BF_4]_2$, where the metal center should be the most electron-withdrawing, the largest J_{PH} couplings are observed. This trend is also confirmed by the comparison of the J_{PH} coupling constants for two Ni complexes: $Ni(MesPH_2)_4$ and $[Ni(MesPH_2)_3(NO)]BF_4$. The latter complex with the acceptor NO group exhibits a substantially larger J_{PH} value (350 Hz versus 283 Hz).

2.6. Molecular dynamics of primary phosphines in solution

It is well known that small chemical entities can undergo dynamic processes in solution such as inversion, hindered rotation or “flip” dynamics. In the case of primary phosphines, while the inversion process does not play an important role [120], hindered rotation was observed in solution or in the gas phase. For example, investigation of hindered rotation of the PH_2 group in phenylphosphine by the means of microwave spectroscopy yielded a two-fold internal rotation barrier of 0.27 kcal mol^{-1}, slightly smaller than the values previously determined from NMR relaxation studies (0.17–1.04 kcal mol^{-1}) and ab initio calculations (1.11 kcal mol^{-1}) [121]. Aliphatic primary phosphines exhibit internal rotation subject to a barrier of the order of 2.0–2.5 kcal mol^{-1} but no inversion were observed in these species [34,120,122,123]. We have recently analyzed the behavior of the ^{31}P NMR signal of the PH_2 fragment in the THF solution of acenaphtene-dibenzobarellenephosphine **21**, in the temperature range from −40 to 80 °C and we have noticed that the PH_2 unit freely rotates above 10 °C, while its rotation is slowed (or even completely blocked) at −40 °C. The barrier to rotation from ^{31}P NMR variable temperature studies is currently under investigation. Parallel quantum chemistry calculations using DFT gave a value of 3.7 kcal mol^{-1}. Several dynamic processes, involving restricted rotation or “flips”, were also observed in organotransition metal complexes of phosphines [83,94,107]. Recently, similar energy barriers in the solid state for the radical R–$PH^\bullet$ species obtained by X-ray irradiation of the dibenzobarrelene phosphines were determined from the density matrix analysis of

Table 3

^{31}P NMR data (δ ^{31}P and J_{PH} (Hz)) for selected primary phosphines and their organotransition metal complexes

Compound	J_{PH} (Hz)	δ ^{31}P	Solvent	References
MePH$_2$	189.9	−161.6	C$_6$D$_6$/THF	[77]
PhPH$_2$	198.5	−121.6	CDCl$_3$	[77]
ArtippPH$_2$	208.0	−139.8	CDCl$_3$	[8]
MesPH$_2$	207.3	−153.9	C$_6$D$_6$/THF	[31,75]
2,4,6-^{i}Pr$_3$C$_6$H$_2$PH$_2$	202.0	−158.6	C$_6$D$_6$	[43,44]
CyPH$_2$	187.0	−111.3	–	[13]
2,4,6-Et$_3$C$_6$H$_2$PH$_2$	203.0	−158.1	C$_6$D$_6$	[43]
2,4,6-Ph$_3$C$_6$H$_2$PH$_2$	201.0	−132.6	C$_6$D$_6$	[43]
DOCPH$_2$	201.0	−156.1	C$_6$D$_6$	[43]
AnthrPH$_2$	206.2	−157.8	CDCl$_3$	[47]
(AnthPH$_2$)$_2$ dimer	196.1	−105.5 (−106.8)	CDCl$_3$	[47]
FcCH$_2$PH$_2$	194.0	−129.1	CDCl$_3$	[69]
2,4-^{t}Bu$_2$-6-^{i}PrC$_6$H$_2$PH$_2$	207.0	−143.9	CDCl$_3$	[38]
2,4-^{t}Bu$_2$-6-MeC$_6$H$_2$PH$_2$	203.0	−143.0	CDCl$_3$	[41,42]
2,4-^{t}Bu$_2$-6-NMe$_2$C$_6$H$_2$PH$_2$	213.7	−141.6	CDCl$_3$	[39]
2,4-^{t}Bu$_2$-6-OMeC$_6$H$_2$PH$_2$	207.4	−155.4	C$_6$D$_6$	[40]
Mes*PH$_2$	210.6 (211.0)	−129.9 (−128.9)	CDCl$_3$	[14]
DippPH$_2$	208.0	−156.4	CDCl$_3$	[45]
DnpPH$_2$	209.0	−139.1, −139.6	CDCl$_3$	[119]
2,6-Mes$_2$-4-MeC$_6$H$_2$PH$_2$	209.8	−147.2	CDCl$_3$	[15]
CMeN(Me)$_2$PhPH$_2$	200.5	−121.95	C$_6$D$_6$	[48]
Cl$_2$C$_6$H$_3$PH$_2$	202.6	−120.7	CDCl$_3$	[49]
C$_6$H$_3$Cl(PH$_2$)$_2$	202.9	−121.9	CDCl$_3$	[49]
C$_6$H$_3$(PH$_2$)$_3$	201.9	−122.5	CDCl$_3$	[49]
(CF$_3$)$_2$C$_6$H$_3$PH$_2$	216.0	−140.0	–	[50]
TrtPH$_2$	189.8	−70.3	Toluene	[61]
DbbPH$_2$	199.0	−143.6	CDCl$_3$	[56]
AndbbPH$_2$	201.0	−150.0	CDCl$_3$	[57]
DpdbbPH$_2$	201.0	−152.0	CDCl$_3$	[58]
TriptPH$_2$	201.6	−156.0	CD$_2$Cl$_2$	[59]
2,3,5,6-Arx$_4$C$_6$(PH$_2$)$_2$	216.8	−130.9	CDCl$_3$	[62]
1,3,5-(2′-EtPH$_2$)$_3$C$_6$H$_3$	195.3	−136.8	CDCl$_3$	[66]
1,3,5-(3′-PrPH$_2$)$_3$C$_6$H$_3$	194.7	−136.1	CDCl$_3$	[66]
1,3,5-(4′-BuPH$_2$)$_3$C$_6$H$_3$	194.7	−136.0	CDCl$_3$	[66]
HN((CH$_2$)$_2$PH$_2$)$_2$	193.0	−147.6	No solvent	[64]
n-BuN((CH$_2$)$_2$PH$_2$)$_2$	190.0	−147.8	No solvent	[64]
p-TolN((CH$_2$)$_2$PH$_2$)$_2$	197.0	−148.2	No solvent	[64]
H$_2$P-(CH$_2$)$_2$(CF$_2$)$_7$CF$_3$	192.0	−136.6	THF	[65]
H$_2$P-(CH$_2$)$_3$(CF$_2$)$_7$CF$_3$	190.0	−139.6	THF	[65]
H$_2$P-(CH$_2$)$_4$(CF$_2$)$_7$CF$_3$	189.0	−139.6	THF	[65]
PhNhCOCH(CH$_2$PH$_2$)$_2$	197.0	−143.0	–	[1]
S(CH$_2$S(CH$_2$)$_3$PH2)$_2$	194.0	−136.3	–	[1]
HOOC(CH$_2$)$_4$C(CH$_2$S(CH$_2$)$_3$PH$_2$)$_2$	193.0	−136.3	–	[1]
33	194.0	−135.6	–	[1]
34	193.0	−135.6	–	[1]
35	194.0	−135.9	–	[1]
36	195.0	−135.6	–	[1]
1,8-Diphosphinenaphthalene	207.7	−104.9	CD$_2$Cl$_2$	[63]
AdPH$_2$	–	−81.6	CDCl$_3$	[90]
Ph(PEt(P(EtPH$_2$)$_2$)$_2$)	191.0	129.0	Toluene-*d$_8$*	[67]
FcPH$_2$	203.0	−143.3	CDCl$_3$	[2]
FcCH$_2$CH$_2$PH$_2$	195.0	−135.8	CDCl$_3$	[2]
1,1′-Fc(PH$_2$)$_2$	–	−143.8	CDCl$_3$	[2]
1,2-Fc(CH$_2$PH$_2$)$_2$	198.0	−127.6	CDCl$_3$	[2]
1,1′-Fc(CH$_2$PH$_2$)$_2$	196.0	−132.0	CDCl$_3$	[2]
PaPH$_2$	214.0	−176.0	C$_6$D$_6$	[104]
[WI$_2$(CO)$_3$(FcCH$_2$PH$_2$)$_2$]	377 (394)	−60.0 (−74.5)	C$_6$D$_6$[a]	[94]
Ni(MesPH$_2$)$_4$	283	−86.5	C$_6$D$_6$	[75]
[Pd(MesPH$_2$)$_4$][BF$_4$]$_2$	422	−73.2	CD$_2$Cl$_2$	[75]
[Cu(MesPH$_2$)$_4$]PF$_6$	317	−121.0	CD$_2$Cl$_2$	[75]
[Ag(MesPH$_2$)$_4$]BF$_4$	297	−131.5	CD$_2$Cl$_2$	[75]
[Ni(MesPH$_2$)$_3$(NO)]BF$_4$	350	−89.7	CD$_2$Cl$_2$	[75]
Ni(triphos)(MesPH$_2$)	281	−96.2	C$_6$D$_6$	[75]
[Cu(triphos)(MesPH$_2$)]PF$_6$	317	−122.0	CD$_2$Cl$_2$	[75]
[Ag(triphos)(MesPH$_2$)]BF$_4$	280	−139.0	CD$_3$NO$_2$	[75]
[Pd(tetraphos)(MesPH$_2$)][BF$_4$]$_2$	381	−94.5	CD$_3$NO$_2$	[75]
BH$_3$ (MesPH$_2$)	370	−68.8	C$_6$D$_6$	[75]
(l-AdPH$_2$)Cr(CO)$_5$	312.81	0.54	–	[90]

Table 3 (*Continued*)

Compound	J_{PH} (Hz)	δ ^{31}P	Solvent	References
(I-AdPH$_2$)Mo(CO)$_5$	308.16	−28.51	–	[90]
(1-AdPH$_2$)W(CO)$_5$	321.00	−47.59	–	[90]
(l-AdPH$_2$)Fe(CO)$_4$	343.69	14.03	–	[90]
(l-AdPH$_2$)Ni(CO)$_3$	298.11	−35.03	–	[90]
[Cp*NbCl$_4$(H$_2$P-^{t}Bu)]	345	22.4	CDCl$_3$	[82]
[Cp*NbCl$_4$(H$_2$P-Ad)]	349	18.1	CDCl$_3$	[82]
[Cp*NbCl$_4$(H$_2$P-Cyc)]	351	9.2	CDCl$_3$	[82]
[Cp*NbCl$_4$(H$_2$P-Ph)]	367	−11.2	CDCl$_3$	[82]
[Cp*NbCl$_4$(H$_2$P-Mes)]	347	−38.7	CDCl$_3$	[82]
[Cp*TaCl$_4$(H$_2$P-^{t}Bu)]	345	21.1	CD$_2$Cl$_2$	[82]
[Cp*TaCl$_4$(H$_2$P-Ad)]	346	17.4	CD$_2$Cl$_2$	[82]
[Cp*TaCl$_4$(H$_2$P-Cyc)]	351	8.9	CD$_2$Cl$_2$	[82]
[Cp*TaCl$_4$(H$_2$P-Ph)]	366	−11.3	CD$_2$Cl$_2$	[82]
[Cp*TaCl$_4$(H$_2$P-Mes)]	360	−39.4	CD$_2$Cl$_2$	[82]
(CyPH$_2$)$_4$Cl$_8$Nb(IV)$_2$	355.6	−2.6	CDCl$_3$	[28]
CyPH$_2$Cl$_5$Nb(V)	347.0	−40.1	CDCl$_3$	[28]
Cp'TaCl$_4$TippPH$_2$	360.9	−35.7	C$_7$D$_8$	[83]
CpNMFe(CO)$_2$MesPH$_2^+$BF$_4^-$	405.8 (407.5)	−60.2	CDCl$_3$	[100]
CyFe(CO)$_2$MesPH$_2^+$BF$_4^-$	400.4	−61.2	CD$_3$CN	[100]
[MnCl(CO)$_3$(PhPH$_2$)$_2$]	–	−14.7	CH$_2$Cl$_2$/CDCl$_3$[b]	[97]
[MnCl(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]	–	−0.8	CH$_2$Cl$_2$/CDCl$_3$[b]	[97]
[MnBr(CO)$_3$(PhPH$_2$)$_2$]	–	−17.3	CH$_2$Cl$_2$/CDCl$_3$[b]	[97]
[MnBr(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]	–	−2.0	CH$_2$Cl$_2$/CDCl$_3$[b]	[97]
OsHCl(MesPH$_2$)(CO)(PPh$_3$)$_2$	340.9	–	CDCl$_3$	[103]
[OsCl(MesPH$_2$)(CO)2(*trans*-PPh$_3$)$_2$]ClO$_4$	421.3	−103.3	CDCl$_3$	[103]
[OsCl(MesPH$_2$)(CO)$_2$(*cis*-PPh3)$_2$]ClO$_4$	423.4	−93.2	CDCl$_3$	[103]
tris(3,4,5-trifluoPhB)^{t}BuPH$_2$	364.0	–	C$_6$D$_5$CD$_3$	[79]
tris(2,6-difluorophenyl)boron^{t}BuPH$_2$	387.0	–	C$_6$D$_5$CD$_3$	[79]
tris(pentafluoropheny1)boron^{t}BuPH$_2$	400.0	–	C$_6$D$_5$CD$_3$	[79]
trans-[RuBr$_2$(PhPH$_2$)$_4$]	–	−25.7	CH$_2$Cl$_2$/CDCl$_3$	[102]
trans-[OsBr$_2$(PhPH$_2$)$_4$]	–	−64.8	CH$_2$Cl$_2$/CDCl$_3$	[102]
fac-Mo(CO)$_3$(HN[(CH$_2$)$_2$-PH$_2$]$_2$)	308.0	−73.4	THF	[64]
fac-Mo(CO)$_3$(*n*BuN[(CH$_2$)$_2$-PH$_2$]$_2$)	309.0	−71.0	Toluene	[64]
cis-Mo(CO)$_4$(*n*BuN[(CH$_2$)$_2$-PH$_2$]$_2$)	313.0	−90.1	THF	[64]
[Au(C6F5)PhPH2]	376.0	−46.0	CDCl$_3$	[106]
[Au(C6F5)3(PhPH2)]	414.0	−59.3	CDCl$_3$	[106]
MePH$_2$·BH$_3$	369.9	−47.0	CDCl$_3$	[77]
^{i}PrPH$_2$·BH$_3$	362.0	−59.6	CDCl$_3$	[78]
PhPH$_2$·BH$_3$	366.6	−66.7	CDCl$_3$	[77]
^{t}BuPH$_2$·B(C$_6$F$_2$H$_3$)$_3$	394.0	–	C$_6$D$_5$CD$_3$	[79]
^{t}BuPH$_2$·B(C$_6$F$_3$H$_2$)$_3$	375.0	–	C$_6$D$_5$CD$_3$	[79]
^{t}BuPH$_2$·B(C$_6$F$_5$)$_3$	318.0	–	C$_6$D$_5$CD$_3$	[79]
1,2-Fc(CH$_2$PH$_2$)$_2$Mo(CO)$_4$	312.0	−78.5	CDCl$_3$	[2]
1,1′-Fc(CH$_2$PH$_2$)$_2$Mo(CO)$_4$	308.0	−79.8	CDCl$_3$	[2]
1,1′-Fc[(CH$_2$PH$_2$Mo(CO)$_5$]$_2$	320.0	−62.5	CDCl$_3$	[2]
1,2-Fc[(CH$_2$PH$_2$Mo(CO)$_5$]$_2$	318.0	−61.4	CDCl$_3$	[2]
W(η-C$_5$H$_4$^{i}Pr)Cl$_3$((C$_3$H$_5$)PH$_2$)(CO)	370.0	−42.9	CH$_2$Cl$_2$/CDCl$_3$[c]	[96]
W(η-C$_5$H$_4$^{i}Pr)Cl$_3$((C$_2$H$_3$)PH$_2$)(CO)	409.0	−43.8	CH$_2$Cl$_2$/CDCl$_3$[c]	[96]
cis-[Cr(CO)$_4$(PhPH$_2$)$_2$]	320.0	−27.5	CH$_2$Cl$_2$/CDCl$_3$[c]	[92]
fac-[Mo(CO)$_3$(PhPH$_2$)$_3$]	320.0	−53.5	CH$_2$Cl$_2$/CDCl$_3$[c]	[92]
cis-[Mo(CO)$_4$(PhPH$_2$)$_2$]	320.0	−60.5	CH$_2$Cl$_2$/CDCl$_3$[c]	[92]
cis-[Mo(CO)$_4${*o*-C$_6$H$_4$(PH$_2$)$_2$}]	320.0	−44.1	CH$_2$Cl$_2$/CDCl$_3$[c]	[92]
fac-[W(CO)$_3$(PhPH$_2$)$_3$]	320.0	−72.0	CH$_2$Cl$_2$/CDCl$_3$[c]	[92]
cis-[W(CO)$_4$(PhPH$_2$)$_2$]	320.0	−80.9	CH$_2$Cl$_2$/CDCl$_3$[c]	[92]
trans-[RuCl$_2$(PhPH$_2$)$_4$]	–	−25.0	CH$_2$Cl$_2$/CDCl$_3$	[101]
trans-[OsCl$_2$(PhPH$_2$)$_4$]	–	−61.4	CH$_2$Cl$_2$/CDCl$_3$	[101]
trans-[RuBr$_2$(PhPH$_2$)$_4$]	–	−25.7	CH$_2$Cl$_2$/CDCl$_3$	[102]
trans-[OsBr$_2$(PhPH$_2$)$_4$]	–	−64.8	CH$_2$Cl$_2$/CDCl$_3$	[102]
Ru^{4}PaPH$_2$	–	−119.0	C$_6$D$_6$	[104]
Ru^4(PaPH$_2$)$_2$	340.8	−102.0	C$_6$D$_6$	[104]
[Cp*RhCl$_2$(Mes*PH$_2$)]	387.0	−43.1	CDCl$_3$	[111]
[Cp*RhCl$_2$(TippPH$_2$)]	386.0	−59.1	CDCl$_3$	[111]
[Cp*CoI$_2$(Mes*PH$_2$)]	382.0	−48.9	CDCl$_3$	[111]
AnthPH$_2$-Os$_3$(CO)$_{11}$(MeCN)	–	−141.0	CD$_2$Cl$_2$	[47]

For some compounds, only chemical shifts were reported. In very few cases, δ ^{31}P was not provided, but J_{PH} was determined from ^{1}H NMR. δ ^{31}P to external H$_3$PO$_4$ reference. All spectra recorded at room temperature unless stated otherwise.

(–): No solvent reported.

[a] At −60 °C.

[b] 7:1 mixture CH$_2$Cl$_2$/CDCl$_3$.

[c] Mixture CH$_2$Cl$_2$/10–15% CDCl$_3$.

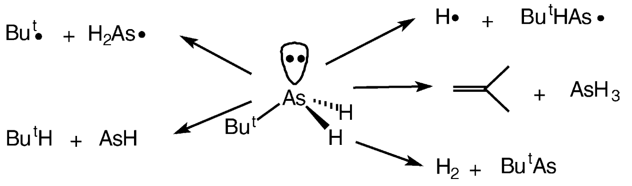


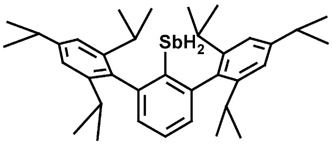
Fig. 5. Schematic representation of the proposed mechanisms [126] for the decomposition of the ^{t}BuAsH_2.

the variable temperature EPR spectra and DFT calculations [58,124,125].

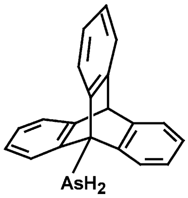
3. Primary arsines and stibines

Arsenic and antimony hydrides are less stable than the corresponding phosphorus compounds. Investigation of the reaction pathways driving the fast decomposition of simple alkyl arsines, for example, led to several possible routes. Cole-Hamilton [126] proposed five distinct mechanisms of decomposition in the case of the ^{t}BuAsH_2 according to the scheme in Fig. 5.

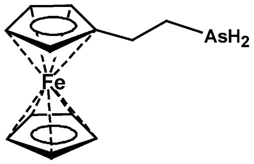
This high instability of the RAsH_2 compounds is responsible for the rarity of the air-stable compounds containing AsH_2 (or SbH_2) group. Apart from the gaseous trihydrides AsH_3 and recently described SbH_3, structurally characterized derivatives of the REH_2 (E = As and Sb) type are very few and until recently, were confined to cases where EH_2 was connected to the same bulky aryl or alkyl ligands already used for the stabilization of the primary phosphines, or in complexes where pnictane hydride is linked to various transition metals. Thermally stable (2,6-Trip$_2$$C_6H_3$)As$H_2$ and (2,6-Trip$_2$$C_6H_3$)Sb$H_2$ **80**, characterized by Power and coworkers [8], are isostructural with the corresponding phosphorus derivative (see Section 2.1.1). As observed by the authors, the increasing lengths of the P–C, As–C and Sb–C bonds in these species almost exactly mirror the differences in covalent radii (P, 1.11 Å; As, 1.21 Å; Sb, 1.43 Å) between these atoms. The melting point of **80** is close to 190 °C (dec. 195 °C), while that of its As analogue is 225 °C.



80



81



82

The intrinsic cage-effect of triptycene was successfully employed to obtain completely air- and moisture-stable TriptAsH_2 **81** in a simple, one-pot synthesis with low yield (11%) [60]. This robust, crystalline primary arsine melts at 293 °C. High symmetry, with the As atom together with two bridging carbons of the barrelene skeleton aligned on the C_3 symmetry axis with a C–As bond distance of 2.170 Å, is observed in its crystal structure. **81** crystallizes in trigonal system in the space group *R*3*c* and shows a pronounced disorder of the As substituents (71.8/28.2%) and an inversion twin ratio (74/26%), characteristic for the pnictogen derivatives of triptycene [60]. The spatial arrangement of the TriptAsH_2 (and also of its PH_2 congener) units in the crystal shows an interesting compact packing (Fig. 6) with all of the triptycene cages parallel by their three-fold axis, and molecules in subsequent layers being rotated by $\pi/3$ around this same axis.

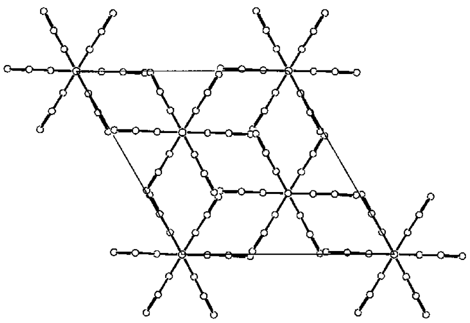


Fig. 6. Crystal packing of the triptycene cages in the crystalline TriptAsH_2 **81**.

A slightly modified synthetic procedure leading to an improved yield (65%) of **81** was also recently reported, together with the structure of a stable TriptSbH_2 derivative [127] (mp 170–172 °C). In their work on ferrocene phosphines, Henderson and Alley obtained a solid, air-stable ferrocenyl primary arsine **82** [2], characterized by a low melting point (44–46 °C). In this compound, the $CH_2CH_2AsH_2$ fragment is approximately coplanar with the Cp ring, and exhibits an As–C bond distance of 1.966(6) Å. The crystalline powder is soluble in hydrocarbons and other organic solvents (except the lower alcohols and DMSO), has the expected unpleasant but mild odor, and easily sublimes under vacuum. One of the rare structurally characterized complexes containing a primary arsine is the pentacarbonyl(phenylarsine) chromium, $C_{11}H_7AsCrO_5$ reported by Huttner and co-workers nearly 20 years ago [128]. In this crystalline material (monoclinic, space group $P2_1/c$), a *trans* influence of the AsH_2 ligand is indicated by the slight difference between axial (1.83 Å) and equatorial (1.88 Å) Cr–C distances. The coordination polyhedron of the Cr atom is an idealized octahedron and the Cr–As distance is 2.462(3) Å.

4. Closing remarks

Although tertiary phosphines are the most extensively used phosphorus ligands throughout inorganic and organometallic chemistry, the rapid development of a range of primary phosphines and their arsenic and antimony analogues is opening avenues for development in the already rich chemistry of these species. This chemistry has developed rapidly in the recent decade due to improvements in the stability and air-inertness of this group of compounds. Recent development of chelating bisphosphines functionalized with small chemical units clearly demonstrates that kinetic stabilization with bulky substituents is not the only way to induce thermal and air-stability at the PH_2 group. Such characteristics enable the use of these species in a growing number of applications. For example, the synthesis of the chiral phosphetanes or phospholanes mentioned earlier in this review are only a few examples of such use. In the future, the development of catalytic and biomedical applications, as exemplified by the use of chiral ferrocenyl phosphine ligands in asymmetric catalysis or preparation of the active antitumor molecules, can be expected to undergo rapid development. In addition, the exponential increase of the availability of the computational theoretical methods makes possible a more detailed description of the electronic structure of these species and will help to better understand and to predict their unusual physical and chemical properties.

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